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FORECASTING ATMOSPHERIC PARTICULATE

SULFUR CONCENTRATIONS USING NATIONAL WEATHER SERVICE

SYNOPTIC CHARTS

A Thesis in

Meteorology

by

Stephen Layton Brueske

Submitted in Partial Fulfillment
of the Requirements
for the Degree of

Master of Science

August 1990

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ABSTRACT

The goal of this research is to increase the understanding of meteorological and chemical mechanisms that control atmospheric particulate sulfur concentrations in the northeastern United States and to develop techniques to forecast atmospheric particulate sulfur concentrations, using standard meteorological charts. Aerosol particles were collected at nine sampling sites and analyzed in steps corresponding to 2-hour time intervals. Atmospheric particulate sulfur concentration variations were found to vary in predictable ways, depending on the synoptic-scale weather system affecting the sampling sites. Insight into how synoptic-scale meteorological processes affect atmospheric particulate sulfur concentrations are developed by this thesis. This information aids in forecasting atmospheric particulate sulfur concentrations and permits better use of current technology to monitor and forecast atmospheric particulate sulfur.

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CHAPTER 1

INTRODUCTION

1.1 Goals and Motivations

The goal of this research is to increase the understanding of meteorological and chemical mechanisms that control atmospheric particulate sulfur (APS) concentrations in the northeastern United States and to develop techniques to forecast APS concentrations using standard meteorological charts.

In the atmosphere, sulfur, in an aerosol form, has a longer lifetime than does sulfur in a gaseous form. The atmospheric lifetime of SO_2 is approximately 1 to 2 days while the atmospheric lifetime of particulate sulfate is typically 3 to 5 days (Rodhe 1978; Shriner et al. 1980, p. 163; Georgii 1982, p. 314). In the northeastern United States gaseous sulfur is mainly SO_2 (sulfur dioxide), while particulate sulfur is primarily NH_4HSO_4 (ammonium bisulfate), and $(NH_4)_2SO_4$ (ammonium sulfate) (Warneck 1988, p. 317). The relatively long residence time and transport distances of atmospheric sulfur aerosols may allow for sulfuric acid deposition far from the sulfur source region. The long residence times of sulfuric acid aerosols may also allow dissolution of trace metals, such as copper or aluminum, before deposition (Winchester 1990). This process is of concern because

deposition of soluble mineral elements may have a greater impact on terrestrial and oceanic ecosystems than deposition of the same elements in an insoluble mineral form (Winchester and Wang 1989). Long residence times may also allow formation of metallic sulfate aerosols, such as cupric sulfate or aluminum sulfate, which when inhaled, may impair human health (Winchester 1983, p. 295; Drummond et al. 1986; Winchester 1988). Therefore, an understanding of the mechanisms which control APS concentrations, combined with an ability to forecast their variations, is necessary to predict and regulate environmental and human exposures to these aerosols.

1.2 EPRI SURE Experiment

This research uses data gathered during October 1977 as part of the Sulfate Regional Experiment (SURE). The SURE was conducted from early 1977 to late 1979 by the Electric Power Research Institute (EPRI), a nonprofit research arm of the U. S. electric utility industry. The SURE involved a program of routine monitoring of air quality over much of the northeastern United States with the goal of defining the relationship between emitted primary pollutants and regional ambient concentrations of secondary products (Mueller and Hidy 1979, p. iii). The SURE concluded that ambient sulfate concentration variations were dominated by meteorological factors (Mueller and Hidy 1982d, p. s-7).

1.3 Synoptic Meteorology

Synoptic scale weather systems can affect atmospheric aerosols via mean vertical motions, horizontal advections and through clouds and precipitation. Within the well-mixed boundary layer (approximately surface to 1 kilometer) air flow is not identically geostrophic and cross-isobar flow is induced by frictional forces. Therefore, the horizontal trajectory of an air parcel around a high or low pressure system will cross isobars from high towards low pressure at an angle between 10 and 60 degrees depending on the vertical mixing of momentum, which in turn depends on the static stability of the atmosphere and the vertical shear of the geostrophic wind. Largest crossing angles will occur during stable situations (i.e. inversions), or when the geostrophic winds aloft are mixed towards the surface, or during cold advection. This cross-isobaric flow causes boundary layer convergence in low pressure regions, resulting in upward vertical motion; this phenomena is known as Ekman pumping.

Upward vertical motions caused by Ekman pumping increase the boundary layer depth, and therefore the mixing depth, thus allowing for greater dilution of local sources of sulfur. Upward vertical motions in low pressure regions also tend to produce clouds, which affect conversion rates of various sulfur compounds in the liquid phase. Clouds may also produce precipitation, thereby providing a wet removal mechanism for

APS. A detailed discussion of in-cloud conversion processes, as well as wet removal processes, is provided later in this paper. High-pressure regions experience effects opposite to those encountered in low-pressure regions. Downward vertical motions decrease the depth of the boundary layer and inhibit cloud formation.

Entire pressure systems also move translationally, typically with an west-to-east component in the mid-latitudes. Therefore, synoptic scale weather systems not only advect air around, and into or out of their centers, they transport entire air masses translationally across the earth's surface.

1.4 Atmospheric Sulfur

Atmospheric sulfur in a gaseous form occurs primarily as SO_2, while atmospheric sulfur in particulate form has been shown to exist primarily as sulfate (Eatough and Hansen 1983). Results of the SURE show that most of the APS in the northeastern United States occurs as sulfate, with more than 80% of the particles smaller than 2.5 μm in aerodynamic diameter. The non-aqueous composition of the fine particles, as expressed in percent of total aerosol mass, was 33-45% sulfate, 1-5% nitrate, 9-12% ammonium, 9 to 23% non-carbonate carbon and 18-40% other inorganic material (Mueller and Hidy 1982b, p. s-8). Throughout the rest of this paper APS will be assumed to be in a sulfate form, with the most likely aerosol

sulfates occurring as either ammonium bisulfate (NH_4HSO_4), ammonium sulfate ($(NH_4)_2SO_4$), or sulfuric acid aerosol (H_2SO_4) (Tanner 1981; Georgii 1982, p. 301; Warneck 1988, p. 317). Sulfuric acid H_2SO_4 has a very low vapor pressure ($<10^{-7}$ atm) under ambient conditions and therefore also exists primarily in the form of particles (Roedel 1979).

One must keep in mind that concentrations of APS discussed in this paper represent actual sulfur concentrations, rather than sulfate concentrations. Therefore, in order to compare sulfate concentrations with APS concentrations discussed in this paper, one must divide the sulfate concentration values by 3 to account for the different molecular weights of sulfate verses sulfur.

1.4.1 Sources of Atmospheric Sulfur

Sea spray, biological decay and combustion of fossil fuels are the primary sources of sulfur-containing compounds in the atmosphere. Typical concentrations of these compounds are listed in table 1.

Natural APS concentrations near the surface in temperate latitudes are approximately 50 ng m^{-3} (Winchester 1983, p. 276). This value is based on studies conducted in relatively clean southern hemispheric regions. The sulfur content of the Earth's crust is too low for soils to provide a significant source of sulfur to the atmosphere, except, perhaps, in local

Table 1 Typical concentrations of common atmospheric sulfur-containing compounds (Seinfeld 1986, p. 9; Warneck 1988, p.486, 518).

COMPOUND NAME	CHEMICAL NAME	CONCENTRATION
sulfur dioxide	SO_2	2-100 ppbv
carbonyl sulfide	COS	400-500 pptv
carbon disulfide	CS_2	10-200 pptv
hydrogen sulfide	H_2S	40-800 pptv
dimethyl sulfide	$(CH_3)_2S$	10-100 pptv
sulfate	SO_4^{2-}	150-50000 ng m^{-3}

areas. Mueller and Hidy (1982d, p. 9-21) estimated the natural land-derived sulfur flux in the SURE study area to account for no more than 1% of the ambient sulfate burden in the SURE study area. The vast majority of the ambient sulfate in the SURE study area was due to anthropogenic input of sulfur-containing compounds, primarily as SO_2, resulting from the combustion of sulfur-containing fuels. Electric utilities and industrial sources accounted for 94% of the SO_2 emissions during the SURE (Mueller and Hidy 1982b, p. s-5). Generally, only small amounts of other sulfur compounds, such as SO_3, H_2SO_4, or sulfate, are emitted simultaneously from these types

of sources (Finlayson-Pitts and Pitts 1986, p. 646). In fact, 90% or more of the sulfur emitted as a result of combustion of sulfur containing fuels is emitted in the form of SO_2, with the remainder emitted primarily in the form of sulfates (Finlayson-Pitts and Pitts 1986, p. 15).

SURE results (Mueller and Hidy 1982b, p.s-5) show seasonal variability in SO_2 emissions to be +/- 15% from the annual mean with maximum concentrations occurring in the winter. Weekend emissions were also approximately 20% less than weekday emissions. However, diurnal concentration fluctuations of SO_2 and sulfate were much larger than emission variations. The highest emissions of SO_2 usually occurred in non-urban areas along the southwest shores of Lake Erie and also extended from southwestern Pennsylvania along the Ohio river to southern Indiana. High emissions also occurred in northern New Jersey and New York City, Kentucky, Tennessee and Alabama (Fig. 1). Analyses of the SURE data clearly showed an association of maximum particulate sulfate concentrations within 100 to 300 km of major SO_2 source areas. On rare occasions the zones of influence may have exceeded 500 km (Mueller and Hidy 1982b, p. vi). Approximately 60 to 70% of SO_2 emissions were injected between 100 and 700 meters above ground while most of the remaining SO_2 entered below 50 meters. Aircraft measurements conducted during the SURE indicated that the highest sulfate concentrations occurred above the level of the ground-based sampling devices. Highest
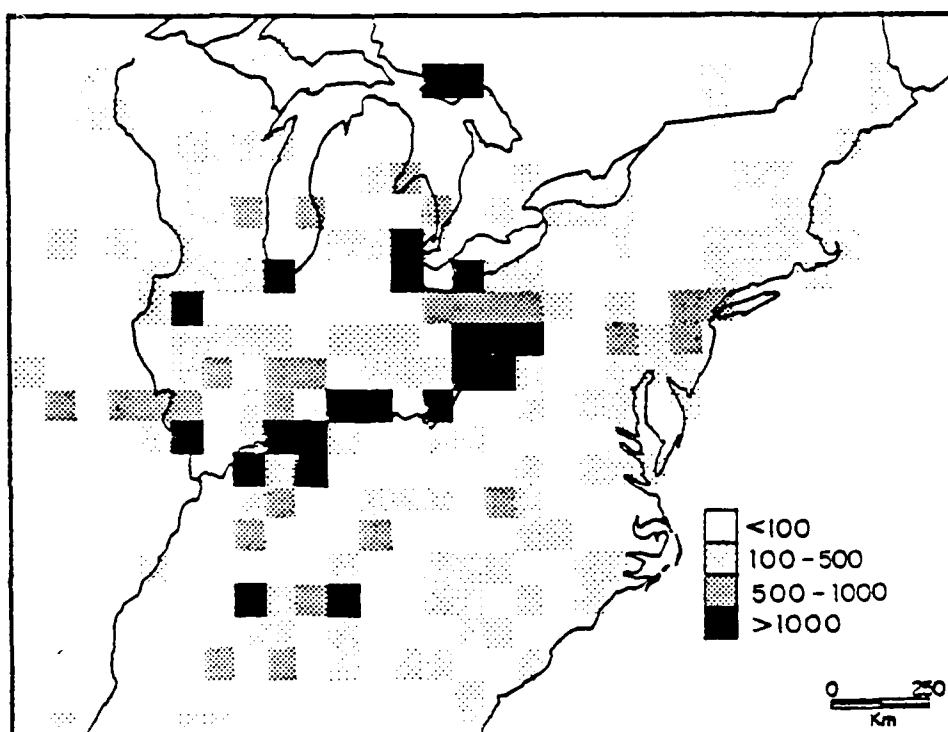
Figure 1 Distribution of SO$_2$ emissions in the SURE area for summer (metric tons/day). Emissions are based on data representative of 1977, from Mueller and Hidy (1982b, p. 5-29).

sulfate concentrations occurred in the layer between 300 and 1500 meters above ground (Mueller and Hidy 1982b, p. s-7).

1.4.2 Factors Affecting Conversion of Sulfur Dioxide to Sulfate

Virtually all of the APS in the northeastern United States is formed by oxidation of SO_2 (Seinfeld 1986, p.657). Oxidation rates of SO_2 are dependent on many factors. These include the presence of oxidants, secondary pollutants and other precursors, sunlight intensity, liquid water, relative humidity and temperature.

Oxidation of SO_2 is generally more rapid in the presence of hydrocarbons, oxides of nitrogen and other secondary pollutants (Finlayson-Pitts and Pitts 1986, p. 647). Therefore, conversion rates often depend on the level of secondary pollutants present in an air mass. Many of these secondary pollutants are photochemically derived, so conversion rates are often dependent on sunlight intensity as well.

Oxidation of SO_2 to sulfate may not be directly photochemical in nature but often involves various oxidants, such as OH or H_2O_2, which have been derived from photochemical reactions. Therefore, oxidation rates are generally higher during daylight than during nighttime, primarily because of the production, and therefore concentration, of OH is highly

dependent on ultraviolet light intensity, and the oxidation of SO_2 to sulfate is primarily a result of gas-to-particle conversion with OH (Warneck 1988, p. 137). However, significant SO_2 to SO_4^{2-} conversion can occur at night, especially in the presence of liquid water in the form of fog or clouds (Finlayson-Pitts and Pitts 1986, p. 647).

The presence of liquid water on atmospheric aerosols, and in clouds and fog, is an important factor in the rate of oxidation of SO_2, because liquid water provides a medium wherein various gases and elements may dissolve. These solubilized gases, and other elements, may then undergo catalyzed reactions, thereby increasing conversion rates of SO_2 to sulfate (Warneck 1988, p. 514). Much higher SO_2 to aerosol sulfate oxidation rates have been observed when a plume passes through a cloud or fog bank (Eatough et al., 1984). Gillani and Wilson (1983) found that local in-cloud conversion rates of SO_2 to sulfate in power plant plumes can be an order of magnitude greater than the average conversion rate in cloud-free air.

Water vapor also has a significant indirect effect on oxidation rates of SO_2. Increased oxidation rates occur at high relative humidities (i.e. greater than approximately 75%) because a layer of liquid water often coats atmospheric particles thereby permitting liquid-phase reactions (Finlayson-Pitts and Pitts 1986, p. 647).

Temperature is important to sulfur chemistry because of

its effect on the rate constants of reactions, as well as its effect on the solubility of gases in aqueous media (Finlayson-Pitts and Pitts 1986, p. 662). Moreover, temperature plays a significant role in determining relative humidity, cloudiness and vertical diffusion. Winchester (1983, p. 280) noted significant correlations between atmospheric sulfur concentrations and temperature, using SURE data at Fort Wayne, IN (site # 7) during October 1977 (the same particulate sulfur data used in this thesis) and temperature observations obtained from a nearby (10 kilometer distant) National Weather Service station. Significant correlations of temperature and APS at other SURE sites were not, however, observed.

SURE results indicate that SO_2 oxidation rates in power plant plumes are generally 0-3% per hour and that these rates appear to be sensitive to background hydrocarbon levels, solar intensity and plume dispersion patterns (Easter et al. 1980a, p. v) While significant, these rates are not fast enough to account for the rapid changes in sulfate concentration observed during the SURE. However, much higher oxidation rates are often observed when a plume passes through a cloud or fog bank (Eatough et al. 1984; Finlayson-Pitts and Pitts 1986, p. 646; Gillani and Wilson 1981).

1.4.3 Conversion Pathways of Sulfur Dioxide to Sulfate

Gas-to-particle conversion of SO_2, via oxidation, is usually the primary source of sulfate in continental areas (Warneck 1988, p. 333). The best known pathway which leads to particle formation is gas-phase oxidation of SO_2 to H_2SO_4 and then partial neutralization of H_2SO_4 by ammonia to form sulfate salts (Warneck 1988, p. 313). The only gas-phase process that is fast and efficient enough to account for the amount of sulfuric acid aerosol observed is the oxidation of SO_2 by the OH radical. Oxidation by other free radicals is believed to be negligible under most atmospheric conditions (Finlayson-Pitts and Pitts 1986, p. 649). This most common oxidation pathway proceeds as follows (Warneck 1988, p. 318):

$$OH + SO_2 + m \longrightarrow HOSO_2 + m$$

$$HOSO_2 + O_2 \longrightarrow SO_3 + HO_2$$

$$SO_3 + H_2O \longrightarrow H_2SO_4$$

$$\text{Net:} \quad OH + SO_2 + O_2 + H_2O \longrightarrow HO_2 + H_2SO_4.$$
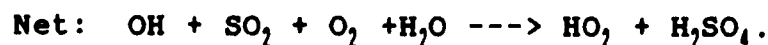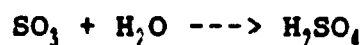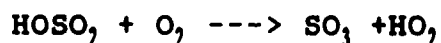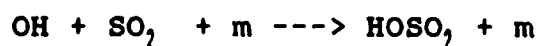
Partial neutralization of H_2SO_4 by NH_3 then forms sulfate salts by the following pathway (Warneck 1988, p. 317):

$$H_2SO_4(H_2O)_n + NH_3 \longrightarrow NH_4HSO_4(H_2O)_{n-1} + H_2O.$$
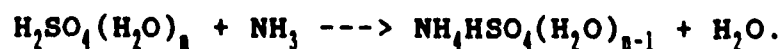
Alternatively, aqueous-phase reactions in raindrops, cloud droplets, and to some extent on liquid coated particles can also provide pathways for conversion of SO_2 to sulfate. Sulfur dioxide is modestly soluble and consequently is absorbed by liquid water. Oxidants, such as H_2O_2 and O_3, may also be solubilized, thereby allowing aqueous-phase oxidation reactions to occur. Clouds, fog and rain have much greater liquid water content than liquid-coated particles and therefore have the potential for contributing more to atmospheric aqueous-phase oxidation (Lamb et al. 1987). Cloud chemistry may be particularly important in atmospheric conditions with vertical motions because ascending air and aerosols may reach the lifting condensation level, at which point clouds, and therefore liquid water, will form and allow the aqueous-phase reactions to proceed. Descent and evaporation may then dry the aerosols, leaving them with different chemical characteristics than they had originally.

Aqueous-phase reactions are relatively fast and under some atmospheric conditions are more important than gas phase reactions (Finlayson-Pitts and Pitts 1986, p. 656). Gillani and Wilson (1983) found that, on average, liquid-phase reactions accounted for 40% or more of the SO_2 to sulfate conversion reactions occurring during the summer in midwestern power plant emissions. They also noted sulfate formation appeared to be particularly rapid in light rain.

The dissolution of SO_2 in water yields SO_2 (aq), HSO_3^-,

SO_3^{2-}. The sum of these species is designated S(IV) (Finlayson-Pitts and Pitts 1986, p. 657). Conversion of S(IV) to sulfate can occur via various oxidizing species, such as dissolved oxygen, O_3, or H_2O_2 (Seinfeld 1986, p.218). H_2O_2 is the most significant oxidant in typical cloud drops and rain (aqueous media with a pH from 2 to 5) and rapidly oxidizes S(IV), primarily because it is easily absorbed into the liquid (Warneck 1988, p. 417) and because it is acid-catalyzed (Martin and Damschen, 1981). The reaction is as follows (Warneck 1988, p. 413):

$$S(IV) + H_2O_2 \longrightarrow SO_4^{2-} + H_2O.$$
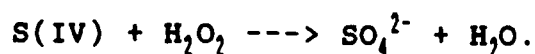
Sulfate containing cloud drops may be transformed to APS if the cloud drop evaporates, leaving a sulfate containing aerosol.

Reactions of SO_2 to sulfate on the surface of particles are normally insignificant unless the particle is coated with liquid water (Finlayson-Pitts and Pitts 1986, p. 647). This is often the case when relative humidities are above approximately 75%. Under such conditions liquid phase reactions occur as discussed above (Warneck 1988, p. 317).

This chapter has reported on the results of past studies which show the importance of meteorological processes in APS concentration variations. The following chapters discuss

various synoptic scale weather systems and their specific effects on APS concentration variations.

CHAPTER 2

PROCEDURES

2.1 Particulate Sampling

Aerosol particles were collected at each of the SURE sites using a "streaker" sampler (Nelson 1977). The streaker sampler consisted of an orifice which moved above a filter strip (Nuclepore, 0.4 μm pore diameter) over the period of a week. Each Nuclepore filter strip therefore contained a time-resolved sample for each week. The streaker sampler operated at flow rates of about 1 l/min. Samples obtained by the streaker samplers were analyzed for elemental composition using Proton induced x-ray emission (PIXE) analysis at Florida State University. Samples were analyzed in steps corresponding to 2-hour time intervals (Johansson et al. 1975).

PIXE analysis is a tool used to determine the concentrations of many elements in very small particulate samples. Although it provides no direct information on the chemical compounds analyzed, it does yield information on the concentrations of various elements which make up the chemical compounds (Warneck 1988, p. 332). Normally the sulfur concentrations obtained by PIXE analysis of filters exposed by the streaker samplers are assumed to represent those of particulate sulfate formed from gaseous SO_2. This assumption

is based on concurrent chemical compound analyses of aerosols obtained during the SURE (Mueller and Hidy 1982b, p. s-8).

Principal component analysis (Preisendorfer 1988, p.11) was used to glean further information about the relative amounts of sulfur in the collected aerosols. Principal component analysis is a statistical procedure which helps summarize the main numerical relationships in large amounts of data. The statistical analysis by itself does not prove cause and effect, nor does it prove physical significance of resolved components. However, with additional information, the significance of the components may be argued. Principal component analysis of the aerosol data showed that most of the sulfur was associated with the sulfate aerosol component and little sulfur was associated with the dust component of the aerosols.

2.2 Classification of Meteorological Categories

Analysis of EPRI-SURE data shows that significant differences in particulate sulfur concentrations occur depending on the synoptic situation. Air masses, fronts and low-pressure systems all influence the particulate sulfur concentration. An understanding of these concentration differences in terms of their chemical and meteorological origins would greatly increase our ability to forecast particulate sulfate concentrations on synoptic time and space

scales.

In order to adequately distinguish chemically different weather events, a number of synoptic-scale phenomena are defined. Stations in the study are characterized as being under the influence of either high pressure, low pressure, high-pressure centers, low-pressure centers, or fronts. Each of these broad categories is further subdivided and discussed in the following pages. Rain and cloud categories were not used because the SURE found little discernable relationship between sulfate variability at ground level and local cloud cover or precipitation (Mueller and Hidy 1982d, p. 9-19). Synoptic-scale weather regimes, air masses and fronts were identified from standard National Weather Service (NWS) 3-hourly surface synoptic charts. Timing of weather events at a specific sampling site were interpolated from the charts rather than obtained from actual station observations. Charts were assumed to be analyzed correctly. This method limits timing errors to less than 3 hours. Thus, the occurrence of weather events (such as frontal passages) are timed to within +/- 1 sulfur sample.

The position of a station relative to synoptic-scale high-pressure and low-pressure systems is distinguished by the curvature of the isobars (as plotted on NWS 3-hourly surface synoptic charts) at a particular stations location. A station is assumed to be under the influence of high pressure when anticyclonic curvature of surface isobars is observed at the

location. Likewise, a station is assumed to be under the influence of low pressure when cyclonic curvature of surface isobars is observed at the station. This distinction is important because of the Ekman pumping associated with high and low pressure.

Stations are considered to be in the center of a high-pressure or low-pressure system if the station is enclosed by the innermost closed isobar on a standard 3-hourly surface synoptic chart. Classification in this way means that a station considered in the center of a high, for example, will have a station pressure no more than 4 mb below the maximum pressure recorded in the particular high-pressure system. Likewise, in the low-pressure case the station pressure will be no more than 4 mb above the minimum recorded station pressure in the particular low-pressure system.

The high-pressure systems (air masses) discussed in this research are classified according to the standard Bergeron classification scheme. The Bergeron scheme categorizes air masses using two or three letter identifiers. The first letter (lower case) distinguishes air masses according to the moisture properties of their source regions. Dry air masses are classified as continental (c) since they are usually formed over relatively dry, continental areas. Likewise, moist air masses are classified as maritime (m) since they usually form in relatively moist, maritime regions. Thus differences in air-mass characteristics are chemically

important because moisture, especially liquid water, can have a significant effect on oxidation rates of SO_2 to sulfate as described in section 1.4.

The second letter identifier (upper case) designates air masses according to the thermal properties of their source regions, such as tropical (T), polar (P) or arctic/antarctic (A). It is important to distinguish differences in air-mass temperature because they have a direct effect on reaction rates and are indicative of parcel trajectories.

Trajectories affect how much SO_2, sulfate, and other pollutants which directly influence production of sulfate, are present in an air mass. As discussed above, atmospheric sulfur is primarily of anthropogenic origin. Therefore, air mass trajectories are important to sulfur concentrations since air masses are representative of their source region not only in temperature and humidity but also in pollution levels. Air flow over SO_2 source regions allows input of SO_2 to an air mass. The SO_2 injected into the air mass may then undergo oxidation, forming APS at a rate which is dependent on the previously mentioned parameters which control gas-to-particle conversion to sulfate.

A further classification can be made using a third letter (lower case) which indicates whether the air mass is cold (k) or warm (w) relative to the surface over which it had moved (Huschke 1959, p. 19). For purposes of this paper the classification of air masses will be restricted to various

combinations of the first two letters in the Bergeron scheme. However, one exception should be noted: Maritime Polar (mP) air that has moved over the Rocky Mountains and dried due to orographic precipitation processes will be classified as modified maritime polar (mP$_m$) air because of the significant differences in moisture content, temperature and source region from that of mP air originating in the Atlantic. Technical definitions of the various air mass types encountered during this study period are provided below.

2.3. Synoptic-Scale Phenomena

2.3.1 High-Pressure Systems

Maritime polar air masses typically form over mid-latitude oceans. For purposes of this study the source region of mP air is the North Atlantic Ocean. Maritime Polar air masses are conditionally stable to stable and typically moist throughout a deep layer, for example from the surface to 700 mb. No mP air masses influenced the SURE study region during October 1977.

Modified maritime polar air masses are mP air masses which have been modified by large-scale vertical motions. Modified maritime polar air masses have undergone orographic ascent with removal of moisture through precipitation. Subsequent subsidence and adiabatic heating results in an air

mass with increased temperature, stability and lower relative humidity than a typical mP air mass.

Modified maritime polar (mP_a) air masses observed in the EPRI-SURE region originate as maritime polar air masses over the North Pacific Ocean. These maritime polar air masses typically separate from a southwest to northeast oriented ridge which extends from off the California coast northeastward into British Columbia. Once the isobars close around the high in British Columbia the maritime polar air masses often move eastward over the Rocky Mountains and modify, as discussed above. The resulting mP_a air masses continue to move eastward, entering the EPRI-SURE study area from the west and northwest, usually following a surface cold front associated with a 500-mb trough.

Maritime tropical air masses have their source region over tropical or subtropical oceans. No purely maritime tropical air masses were observed in the study area during October 1977.

Continental polar air masses have source regions over high latitude land areas or pack ice. The continental polar air masses observed in this study originate in eastern Alaska and northern Canada. They are typically dry, relatively cold, and stable to conditionally unstable.

2.3.2 Low-Pressure Systems

For purposes of this paper, low-pressure systems are differentiated according to their direction of travel and their formation mechanisms.

Southeast Movers (SEM) are cyclones which form in polar regions and move southeastward, entering the SURE study area from the northwest. These cyclones move with the 500 mb flow west of a long-wave trough and are characteristically surrounded by cold air. During this study, several SEMs formed in Alaska and northern Canada.

Lee cyclones (LEE) form as a result of orographically induced cyclogenesis on the lee side of the Rocky mountains. These lows typically form in the Oklahoma and Texas region and move northeastward, entering the SURE study area from the southwest.

Coastal cyclones (COA) typically form in the baroclinic zone along the eastern seaboard and move northeastward. These cyclones move with the 500 mb flow east of a long-wave trough and are characteristically surrounded by warm air. Coastal lows typically exhibit large pressure gradients, and therefore strong winds. They often strongly influence the eastern portion of the SURE study region by advecting air inland off the Atlantic Ocean to the north of the coastal cyclone's center.

Northeast Movers (NEM) are cyclones which form in the

northwestern Gulf of Mexico and travel northeastward ahead of a 500 mb long-wave trough, entering the SURE study area from the southwest. They are characteristically surrounded by relatively warm, moist air and rapidly advect warm, moist air from the Gulf of Mexico into the SURE study area.

2.3.3 Fronts

A front is the interface, or transition zone, between two air masses of different thermal or moisture characteristics. The vertical motion of air near a front depends on the relative densities of the two air masses. Temperature distribution is the most important regulator of atmospheric density, therefore, a front usually separates air masses of different temperatures.

A cold front (CF) is a front that moves so that colder air replaces warmer air. The air ahead of a cold front is not only warmer, but typically contains more water vapor than air behind the front. Deep precipitating convection is common along a cold front.

A warm front is a front that moves so that warmer air replaces colder air. Surface warm-front locations are often difficult to identify because warm fronts are generally associated with gradual air mass transitions. Very few easily identifiable warm fronts occurred in the SURE region during

October, 1977. Therefore, no conclusions or discussions of them will be presented.

CHAPTER 3

RESULTS AND DISCUSSION

3.1 Meteorological Setting

Geographic location and surface synoptic weather phenomena directly influence the concentration of APS at a given site. The various sampling sites are therefore categorized as continental or coastal locations. Fig. 2 shows the location of the 9 sampling sites and table 2 further describes the stations location and site number.

The data are also grouped according to the surface synoptic weather events affecting the sampling site at a given time. The differences in particulate sulfur concentration caused by various locations and surface synoptic weather events are discussed in detail below.

The sampling sites used in this study are grouped into continental or coastal locations because the variations in synoptic scale weather events, and the chemical response to these events, is greater between the two regions than within the two regions. Stations 4, 5, 6 and 7 are considered continental locations because they are primarily under the influence of continental synoptic weather events throughout the study period. Likewise stations 1, 2 and 3 are considered coastal locations since they are primarily influenced by coastal synoptic weather events throughout the study period.
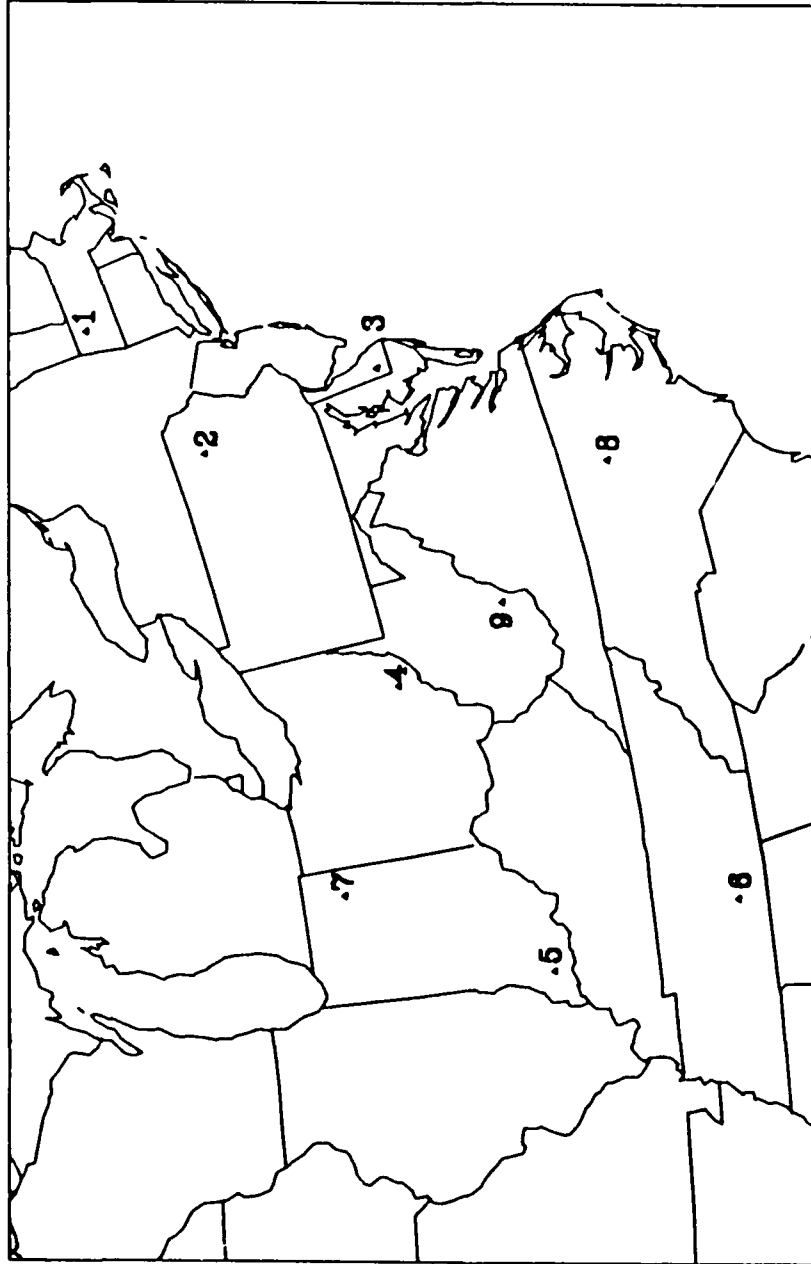
Figure 2 Location of SURE sampling stations, from Mueller and Hidy (1982a, p. 1-2).

Table 2 Location of SURE Sampling Stations (Mueller and Hidy 1982a, p. 1-1)

Site Number	Station Name	Direction from City to Site	Distance from City (miles)	City
1	Montague	N SE	15 5	Amherst, MA Greenfield, MA
2	Scranton	NW	25	Scranton, PA
3	Indian River	ESE	4	Millsboro, DE
4	Duncan Falls	SE	8	Zanesville, OH
5	Rockport	W N	0.5 8	Rockport, KY Owensboro, KY
6	Giles County	SSE NW NE	24 42 10	Columbia, TN Huntsville, AL Pulaski, TN
7	Ft. Wayne	SW	15	Ft. Wayne, IN
8	Research Triangle Park	SE NW	7 10	Durham, NC Raleigh, NC
9	Lewisburg	E SW	5 2	Lewisburg, WV White Sulfur Springs, WV

Stations 8 and 9 are significantly influenced by both continental and coastal synoptic weather events and will be discussed in the appropriate context.

Three distinct upper air weather regimes can be distinguished during the study period by considering the location of the polar front jet stream. These upper air weather regimes indirectly influence surface particulate sulfur concentrations because they influence the movement of various synoptic weather phenomena. The first jet stream pattern is low zonal (i.e the jet was oriented primarily west to east and is fairly far south). It occurred from the beginning of the study period until 10 October. The second jet stream pattern is meridional (i.e., the jet had a strong north and south orientation). This pattern occurred from 11 October through 20 October. The third jet stream pattern is high zonal (i.e. the jet was oriented west to east, but far north of the SURE stations) and occurred from 21 October to the end of the study period. These various jet stream patterns and locations are important because of their influence on cyclone tracks which, in turn, affect surface mixing and trajectories.

Cyclones typically move along the polar jet stream. In the low zonal polar jet stream regime, lee cyclones typically formed in Oklahoma and Texas and moved along the southern edge of the polar jet stream east-northeastward through the SURE study region, while the 500-mb cyclone centers typically

passed north of the SURE study region. In the meridional jet stream regime the jet stream again remained over the SURE region and deep 500-mb troughs and 500-mb low centers passed over the SURE area. Southeast moving cyclones entered the SURE region from the central Canada and moved southeastward on the western side of 500-mb troughs. Coastal cyclones formed and moved northeastward up the eastern side of 500-mb troughs. During the third jet stream regime, the jet stream was north of the SURE region so that most cyclones and fronts passed north of the SURE region. Therefore lighter winds and reduced mechanical mixing occurred during this time. This reduction permitted easier nighttime decoupling of the surface layer from the residual mixed layer and was therefore more conducive to formation of diurnal cycles of APS concentrations. However, a coastal cyclone did affect the most southeastern sampling stations (sites 8 and 9) from 25 October to 29 October.

3.2 Diurnal Effects

Diurnal cycles of APS concentration are most readily apparent in continental locations, especially when these stations are south of the polar jet stream and primary storm tracks. The diurnal cycles are much less apparent at coastal locations. APS concentrations in anticyclones exhibited significant diurnal behavior at most of the sampling locations

while APS concentrations in cyclones typically exhibit insignificant diurnal behavior at most of the sampling locations. The observed behavior of APS, and the reasons for the behavior of APS, under various synoptic conditions and at various locations is discussed below.

Diurnal cycles of APS concentration arise from variations in surface-layer mixing and gravitational settling of particulate sulfur, as well as variations in photochemical reaction rates. Surface-layer mixing occurs via buoyant or mechanical processes, while removal of particulate sulfur by gravitational settling predominates in the absence of surface-layer mixing, when the surface air becomes decoupled from the free troposphere. Since the formation of sulfate is most frequently a result of gas-to-particle reactions involving the OH radical, large and rapid diurnal changes in OH radical concentration may also result in diurnal variations of atmospheric sulfate. Details of these two mechanisms, and their relation to the observed patterns of occurrence of diurnal cycles, are discussed below.

Diurnal cycles of APS are readily apparent at continental sampling locations (sites 4, 5, 6 and 7) throughout most of the study period and occurred primarily in anticyclones. Daily atmospheric sulfur concentration levels typically reached a minimum between 0000 and 0800 Eastern Daylight Time (EDT) and a maximum between 1200 and 1600 EDT. In contrast, such events are rare at the coastal sampling locations (sites

1, 2 and 3). Moreover, the diurnal cycles are more evident in stations further from the polar jet stream and storm tracks. For example, diurnal variations are more evident at the northern continental stations (sites 4 and 7) after October 21 when the polar jet stream and storm tracks are north of these stations.

3.2.1 Surface Mixing vs. Gravitational Settling

Surface-layer mixing via buoyant or mechanical forcing is important in counteracting gravitational settling of particulate matter. Deposition velocities of particulate sulfate have been measured and typically range from 0.17 to 1.2 cm s^{-1} (Finlayson-Pitts and Pitts 1986, p.705). Therefore, only when turbulent vertical velocities are relatively small can gravitational settling significantly affect the surface layer APS concentration on a time scale of hours. Thus, the effects of gravitational settling should be limited to those periods with little buoyant or mechanical mixing.

Buoyant mixing of the surface layer occurs as a result of surface heating. As the sun warms the earth, heat is transferred to the air nearest the surface making the surface layer warmer, and therefore less dense, than the air above it. This destabilization results in, and is limited by, vertical mixing. Thus, buoyant mixing counteracts gravitational settling and tends to keep particulate sulfur uniformly mixed

throughout the boundary layer. During daylight hours, especially in high-pressure, areas where skies are predominately cloud free, surface heating creates buoyant overturning within the boundary layer which maintains the turbulent transports necessary to offset gravitational settling.

Gravitational settling will occur in the absence of either buoyant or mechanical mixing. Decoupling of the surface layer from the residual of the well-mixed diurnal boundary layer allows settling of surface layer particulate matter, thereby lowering the surface layer particulate sulfur concentration. Decoupling of the surface layer from the residual layer will occur when diurnal boundary layer convection ceases for the night. Thus, gravitational settling should act to reduce surface layer particulate sulfate concentrations at night.

During daylight hours, especially in high-pressure systems where skies are usually cloud free, surface heating creates buoyant overturning of the atmosphere which destroys nocturnally created inversions. Thus, under clear daytime conditions, or windy conditions anytime, turbulent transport offsets gravitational settling and also mixes air with higher concentrations of particulate sulfur from aloft to the surface.

High APS concentrations do not typically originate from dust related sulfur raised from the surface. Principal

component analysis (Preisendorfer 1988, p. 11) of the aerosol data showed that most of the sulfur was associated with the sulfate aerosol component and little sulfur was associated with the dust component of the aerosols. An example of the amount of sulfur found on the dust component compared to sulfur on the particulate sulfur component is found in Fig. 3. Similar ratios of sulfur associated with the sulfate aerosol component to sulfur associated with the dust component are observed at all of the SURE sites. This finding rules out variations in suspended dust as a reason for diurnal cycles of particulate sulfate.

Gravitational settling of APS occurs on calm nights when neither buoyant nor mechanical turbulence is present. Calm nights frequently occur during high-pressure regimes and this is the time when diurnal cycles are observed in this study. Windy conditions, and the associated surface layer mechanical mixing, eliminate the gravitational settling contribution to the diurnal cycle. This situation is typically associated with the presence of a jet stream over the site. This relationship results from the close physical link between the jet stream and both cyclonic wind systems and rapidly translating anticyclonic air masses.
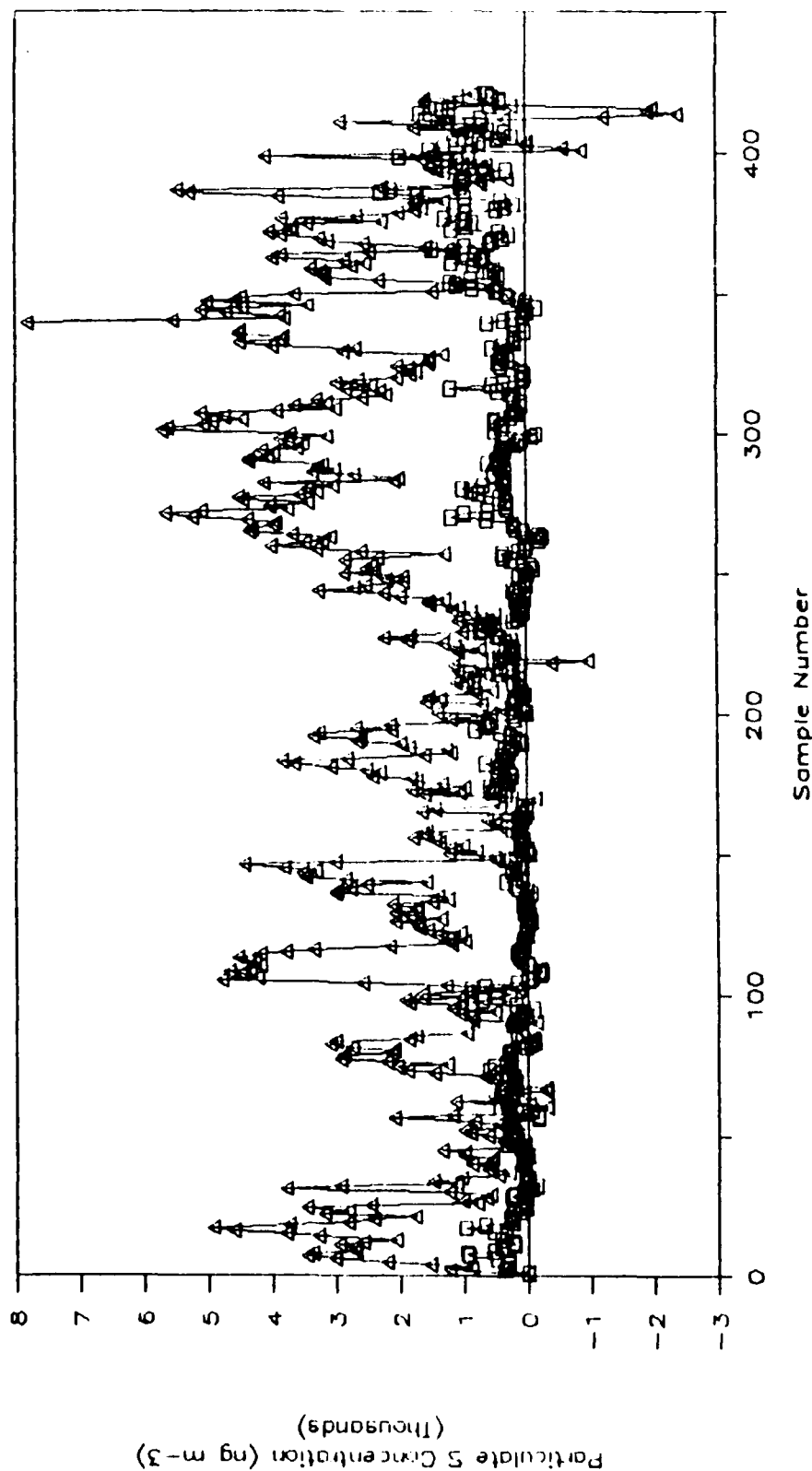
Figure 3   Results of principal component analysis of all 2-hourly samples
taken from 29 Sep. - 3 Nov., 1977 at Duncan Falls, OH (site 4).
Concentrations of sulfur associated with the particulate sulfur
aerosol component are plotted as ▲. Concentrations of sulfur
associated with the dust component are plotted as □. The
occasional negative concentrations are an artifact of the
statistical methods employed and do not represent reality.

3.2.2 Photochemical Reactions

Photochemical reactions produce the chemical precursors necessary for oxidation of SO_2 to sulfate. Earlier in this paper the OH radical was mentioned as the most common oxidizing agent for SO_2. The OH radical is highly dependent on sunlight for its formation and is rapidly removed from the atmosphere by reactions with many trace gases. Therefore, OH exhibits large and rapid diurnal variations in concentration, with the highest concentrations occurring at mid-day (highest UV light intensity) and the lowest concentrations (virtually zero) occurring a few hours after sunset (Warneck 1988, p. 137). Rapid production of sulfate via reactions m ntioned in section 1.4.3 may cause a rapid increase in daytime concentrations of APS. The lack of this form of sulfate production at night would eliminate one of the major production mechanisms of APS. Therefore, photochemical reactions may be responsible for the rapid daytime rise in APS concentrations which most frequently occur during situations conducive to photochemical activity (i.e., clear-sky situations observed when a station is under the influence of an anticyclone).

3.3 Synoptic Scale Effects

Various synoptic-scale weather systems influence APS concentrations by controlling the advection of air into the SURE region. Air advected into the SURE region from the north typically arrives via central and eastern Canada. This air is cooler, drier and often has experienced less emissions of SO_2 and other pollutants than air advected from the south. Thus, it is not conducive to rapid APS formation. In contrast, air advected from the south typically comes from the southeastern United States and Gulf of Mexico. This air is typically warmer, moister, has experienced more emissions of SO_2 and other pollutants and has spent time in a region of greater ultraviolet light intensity. All these factors create a chemical environment which is more efficient at production of APS. Thus, synoptic-scale weather patterns control both air trajectories and chemical environments which contribute to the observed APS gradients. Various synoptic weather patterns and their effect on APS concentrations are discussed below. Mesoscale effects that occur in conjunction with synoptic-scale events, such as cold fronts associated with cyclones, are discussed separately in section 3.4.

3.3.1 Sulfur Concentration Patterns in Anticyclones

Northern-hemispheric anticyclones, because of the clockwise air circulations around them, tend to have higher temperatures, higher dew points, and higher pollution levels on their west sides than on their east sides. These conditions lead to higher concentrations of APS on the western sides of anticyclones than on their eastern sides. However, differences do exist between various types of anticyclones and these differences are discussed below.

Atmospheric particulate sulfur concentrations at both continental and coastal locations tended to increase from the eastern to western edges of mP_a anticyclones whose centers passed over the sampling site (e.g., Fig. A.3, 10-11 Oct.; Fig. A.21, 9-10 Oct.; Fig. A.40, 19-21 Oct.). The APS gradient across a typical mP_a anticyclone occurs as a result of meridional advection of APS, as well as the existence of a chemical environment better suited to rapid production of APS on the western side of an anticyclone than that on the eastern side. The eastern side of a typical mP_a anticyclone has winds from the north and therefore advects any atmospheric aerosols from a relatively clean, cool northern region towards the south. Likewise, winds with a southerly component occur on the western side of anticyclones, thereby advecting warmer and moister air from south to the north.

Modified maritime polar anticyclones whose centers did

not pass over the sampling sites typically had the centers pass north of the SURE region. Passage of these anticyclones, at both continental and coastal locations, yielded little change in APS concentration, or an actual decrease in concentration from the beginning to the end of the anticyclone period (e.g., Fig. A.9, 12-13 Oct.; Fig. A.23, 22-25 Oct.; Fig. A.48, 29 Oct.- 2 Nov.). This decrease probably occurred because anticyclone centers which passed north of the SURE region typically caused less meridional advections in the region, but stronger east to west winds. mP_a anticyclones whose centers passed north of the SURE region typically advected air into the region from the east. This air had usually spent a great deal of time over the Atlantic ocean. As the anticyclone left the sampling stations, the concentrations remained relatively constant, probably due to the constant fetch of air over pollutant sources.

Modified maritime polar air masses exhibited strong diurnal variations of APS at continental locations (e.g., Fig. A.24, 29 Oct.- 3 Nov.; Fig. A.28, 19-21 Oct.). Diurnal concentration variations of APS are much less evident at both coastal stations (sites 1,2 and 3) and transition stations (sites 8 and 9).

Only two cP anticyclones entered the SURE region during the study period. Low particulate-sulfur concentrations occurred in continental cP anticyclones because of their source region, the trajectories around the air mass and the

chemical environment of the air mass (e.g., Fig. A.26, 2-5 Oc..). cP air-masses formed in high-latitude environments, which are typically low in sources of SO_2, and therefore initially contain few sulfur compounds. Thus, low initial concentrations of SO_2, combined with low temperature, low relative humidity and low ultraviolet light intensity, created a chemical environment unfavorable for rapid gas-to-particle conversion of SO_2 to sulfate. This unfavorable chemical environment even extended to the southern most sampling stations, which were often directly downwind of the Ohio Valley, a region of high SO_2 emissions (e.g., Fig. A.32, 2-5 Oct.). Despite a major input of SO_2 into many cP air masses before they reach the southern sampling stations, APS concentrations remained low because of the unfavorable chemical environment.

Continental polar air masses, at both continental and coastal locations, usually exhibited an east to west gradient of APS, with APS concentrations typically increasing 80% to 90% from the eastern to western edge of cP anticyclones (e.g., Fig. A.2, 3-5 Oct.; Fig. A.38, 2-5 and 6-7 Oct.). Typical APS concentrations were initially 1,000 to 3,000 ng m^{-3} on the eastern edge of the cP anticyclone and rose fairly uniformly to 3,000 to 6,000 ng m^{-3} on the western edge of the anticyclone. For example, APS concentrations approximately doubled from the eastern to western side of the cP anticyclone observed at Giles City (Fig. A.32, 2-6 Oct.). There are,

however, a few exceptions observed during this study (e.g., Fig. A.14. 7-8 Oct.; Fig. A.26, 2-6 Oct.; Fig. A.44, 7-8 Oct.).

Coastal cP anticyclones typically exhibited an APS concentration gradient, with lowest concentrations on their eastern edges and highest concentrations on their western edges (e.g., Fig. A.2, 4-5 Oct.; Fig. A.8, 4-5 and 6-8 Oct.). The increase in APS concentration across a typical coastal cP anticyclone was most likely caused by large modifications of the northward flowing air on the western side of the anticyclone. This air had typically traveled from the Southeastern United States out over the Atlantic Ocean where it had warmed and moistened before reentering the Northeastern United States. Therefore, the chemical environment of the air mass was more conducive to rapid SO_2 to sulfate conversion on its western than eastern side.

Within cP anticyclones, diurnal trends were not very evident at either continental or coastal locations. The lack of a diurnal trend was probably due to the relatively clean, dry and cool nature of the cP air masses, which inhibited rapid chemical production of APS. Giles City (Fig. A.32, 2-6 Oct.) was the exception; diurnal trends were evident throughout most of the sampling period. This unique feature may have been a result of Giles City being the most southerly station, thereby allowing for the greatest modification of the cP air mass before it reached the station.

3.3.2 Sulfur Concentration Patterns in Cyclones

North American cyclones, because of the counterclockwise air circulations around them, tend to have higher temperatures, higher dew points, and higher pollution levels on their eastern sides than on their western sides. These conditions lead to higher concentrations of APS on the eastern sides of cyclones than on their western sides. However, differences do exist between various types of cyclones and these differences are discussed below. Cyclone centers very rarely passed over the sampling stations. When they did, particulate sulfur concentrations in cyclones were usually higher at the beginning stage of the low pressure influence. The reasons for this gradient are discussed in more detail in the section on cold fronts.

There were significant differences between continental and coastal cyclones. Pressure gradients were significantly greater in the coastal cyclone events observed during this sampling period than in the continental cyclone events. Coastal cyclonic pressure centers quite frequently passed over sampling stations while continental type cyclonic pressure centers rarely moved over sampling station locations. This difference was significant because greater mixing occurs in the most intense pressure gradient areas and in the centers of cyclones because of the enhanced wind, Ekman pumping and resultant moist convection. Trajectories around continental

verses coastal cyclones are also important in determining APS concentration. Continental type cyclonic trajectories typically came from cooler, drier and often less polluted areas than trajectories around coastal cyclones. Coastal cyclones therefore had air which was typically warmer, more moist and more polluted than that of continental cyclones. This allowed increased conversion rates of SO_2 to particulate sulfur. However, the increased mixing and removal of APS via wet deposition processes kept APS concentrations low in coastal cyclones. The erratic nature of particulate sulfur concentrations in cyclones may have been caused by patchy rainout, or the deformation of air mass boundaries near the spiral circulation center.

Lee cyclones appeared to have similar APS concentration patterns at both continental and coastal locations. A single LEE cyclone center passed over four of the sampling stations (sites 1,2,4 and 7) during the last days of September and the first few days of October. All four of these stations recorded APS concentration decreases of approximately 50% to 60% from the beginning to the end of the influence of the LEE cyclone (e.g., Fig. A.38, 1-2 Oct.). These concentration decreases probably occurred because of the advection and temperature patterns described above.

The majority of LEE cyclone centers did not pass over the sampling station but rather passed to the northwest of the SURE network. In these cases APS concentration patterns

behaved in a highly erratic manner. Some APS concentration levels increased, some decreased and some remained relatively constant. These concentration variations are most likely caused by patchy rainout of APS and vigorous mixing of the air mass via convection. Diurnal APS concentration variations are not usually evident in LEE cyclones, although some cases did occur (e.g., Fig. A.19, 30 Sep.).

Only one NEM cyclone influenced the SURE study area during the period of this study (it influenced 7 of the 9 stations for 1 to 2 days). During this period no diurnal variations were evident at any of the sampling locations. The NEM which influenced the stations caused extensive and heavy precipitation (.25 to >1 inch in 24 hours) at sites 3, 5 and 6. Removal of APS by rainout may have been responsible for the rapid drop that occurred at site 5 on 26 October, 0200 local time (Fig. A.29;) and site 6 on 25 October 1400 local time (Fig. A.35). However, no general conclusions about the effects of this cyclone type can be drawn from this single case.

Continental locations measured higher APS concentration levels on the eastern edge of SEM cyclones than on the western sides. Decreases in APS concentration of approximately 40% to 60% occurred from the beginning to the end of the influence of SEMs at continental locations.

Sites 8 and 9 were only slightly influenced by SEMs. By the time SEMs arrived at sites 8 and 9 they behaved more like

a cold front, since the pressure trough which passed over the station was far removed from the cyclone center (Fig. A.45, 11-12 Oct.). Concentrations of APS in these cases varied little except for a rapid and sudden concentration drop at frontal passage. This is similar to patterns observed in cold fronts, which are discussed below.

Concentrations of APS did not appear to be significantly influenced by SEM cyclones at coastal locations. Southeast moving cyclones often weakened (i.e., their central pressures rose) as they moved across the SURE region. Once these SEM cyclones moved into the baroclinic zone along the east coast they often reintensified and transformed into COA cyclones. Significant diurnal APS concentration variations did not occur at any of the stations effected by SEM cyclones.

Purely continental locations were not influenced by COA cyclones during this study period. However, COA cyclones frequently affected sites 1,2,3,8 and 9. All of these stations recorded some of their lowest APS concentrations during COA events (e.g., Fig. A.4, 15 Oct.; Fig. A.10, 16 Oct.; Fig. A.47, 26 Oct.), especially when COA centers passed directly over the sampling stations. These low APS concentrations were most likely a result of rainout of APS by frequent and intense precipitation, intense boundary-layer mixing, and entrainment of relatively clean air from the Atlantic Ocean. Diurnal APS concentration variations were not observed at any of the locations influenced by COA cyclones.

3.4 Frontal Effects

Fronts are transition zones between two air masses with different thermal or moisture characteristics. These differing air mass characteristics on either side of a front often form narrow zones of large APS gradients. Diurnal concentration variations may, at times, occur in phase with a frontal passage and further enhance APS gradients across a front. Variations in APS concentration in and across frontal zones are discussed below.

3.4.1 Cold Fronts

A sharp APS concentration maximum was observed near cold fronts, with rapid APS concentration decreases occurring after frontal passage (e.g., Fig. A.2, 6 Oct.; Fig. A.16, 16 Oct.; Fig. A. 21, 11 Oct.; Fig. A.33, 11 Oct.; Fig. A.50, 2 Oct.). The sharp APS concentration maximum was probably caused by increased particulate sulfur formation in the "warm conveyer belt" (Carlson 1980) region ahead of the cold front. The air that made the warm conveyor belt was typically advected from the southern United States, a region of high temperatures, high moisture contents and high ultraviolet sunlight intensities. Such conditions were conducive to rapid particulate sulfate formation. Moreover, the air masses feeding the warm conveyor belt had frequently passed over

significant sulfur source regions lying to the south before turning back towards the north. Aqueous-phase reactions in the nonprecipitating stratus and cumulus clouds, which are common in prefrontal air, also contributed to enhanced APS concentrations. Thus both source exposure and chemical environment was particularly favorable in the warm, northward flowing, pre-frontal air. Particulate sulfur concentrations often decreased drastically shortly after cold frontal passage. This decrease was most likely caused by the influx of cold, dry and clean air which followed behind the cold front.

3.4.2 Warm Fronts

Only one case of surface warm frontal passage was easily identifiable in this study. Therefore, APS concentration variations in response to warm fronts are not investigated in this paper. Hales (1989) describes a model that he developed to represent various atmospheric chemical responses to typical weather systems. He described the effects that a typical warm front would have on APS concentrations. Hale's model predicts maximum cloud and air sulfate concentrations to occur 150 km to 200 km ahead of a typical warm front and at a level approximately 500 m above ground.

CHAPTER 4

CONCLUSIONS

Atmospheric particulate sulfur concentrations are a result of atmospheric transport over long time and distance scales, rather than short-range advection. Atmospheric particulate sulfur concentrations depend on the characteristics of the air masses, as opposed to direct advection from SO_2 sources. Downwind from the Ohio valley, a major source region of SO_2, the particulate sulfur concentration varies more by air mass differences than by the specific locations of the sampling sites downwind of the major SO_2 source region. Therefore, local gas-to-particle conversion is usually not the reason that high particulate sulfur concentrations are found at a given time and place. Rather, the synoptic-scale history of the air mass is the dominant factor.

Slow gas-to-particle conversion rates within unfavorable chemical environments (e.g., few clouds, low humidity, low temperatures, low ultraviolet sunlight intensity) allow time for widespread dilution and dispersion of SO_2 without significant reaction. Indeed, advection distances on the order of 1200 km are possible for particulate sulfate assuming a combined atmospheric lifetime of SO_2 and APS of 4 to 5 days and average planetary boundary layer wind speeds of 10 m/s. For example, much of the particulate sulfur measured in the

Ohio river valley may be of Ohio river valley SO_2 origin, having traveled into the southeastern United States, been processed into atmospheric particles and then transported back into the Ohio river valley, in the warm, often cloudy region ahead of a cold front. Thus, SO_2 emitted in the Ohio valley may be transported to areas with more efficient gas-to-particle conversion rates, followed by a return of the resulting particles to their original source region.

Air advected into the SURE region from the north is fairly clean because there are few pollutant sources in the air mass source region and because there is little gas-to-particle conversion of any SO_2 that is emitted into the air mass. Conversely, air advected from the south has often traveled around a high pressure system, first moving over a high SO_2 emission region and picking up SO_2. This air is then brought into the southeastern United States where the chemical environment becomes more conducive to rapid particle formation. The 4 to 5 day residence time of particles then allows them to be advected northward ahead of a cold front in the warm, moist northward flowing air on the west side of a typical anticyclone. This is also a region of rapid gas-to-particle conversion. Therefore, rapid particle formation, combined with relatively low dry-deposition fluxes, allow high concentrations of particulate sulfur to prevail in the air ahead of cold fronts. Particle washout in frontal precipitation and air mass replacement by the clean, cool air

behind a typical cold front results in dramatically lower particulate sulfur concentrations behind the front. This sharp drop in particulate sulfur concentration across a cold front is typically 60% +/- 20% of the prefrontal value.

Concentration variations of APS are principally caused by changing meteorological phenomena occurring on scales large enough to be observed by the present synoptic meteorological network and to be forecast using meteorological data available from current numerical weather prediction (NWP) models.

Diurnal variations in the surface-layer particulate sulfur concentrations appear to be primarily a result of removal of particulate sulfur by nocturnal gravitational settling during light wind conditions. Higher daytime (windy) concentrations result from buoyant (mechanical) mixing which compensates for dry deposition.

Synoptic-scale variations of particulate sulfur aerosol result from different air masses passing over the sampling site. Air mass source regions determine air mass characteristics, such as temperature, moisture content and availability of various chemical precursors. These in turn affect chemical conversion rates of SO_2 to particulate sulfur. The recurrence of similar synoptic scale meteorological phenomena results in the recurrence of similar particulate sulfur concentration patterns.

A thorough understanding of the relationship between synoptic scale meteorology and APS concentrations can be used

to both forecast particulate sulfur concentrations and to design the efficient large scale sampling networks necessary to accurately predict deposition of particulate sulfur.

Appendix A

Atmospheric Particulate Sulfur Concentration Graphs

This appendix contains time-series graphs of APS concentration from the 9 stations described in the text. The following symbols are used to define and delineate between differing air masses and are placed on or above and below the time line (represented as ━━━━━━━━) at the top of each graph. The weather phenomena are described in the text.

	Indicates a change in weather phenomena at a station.
┣━━┫	Indicates the center of a weather system is at a station.
⟩	Indicates cold frontal passage at a station.
CF	Indicates cold frontal influence at a station.
cP	Indicates continental polar anticyclone at station.
mPm	Indicates modified maritime polar anticyclone at station.
LEE	Indicates lee cyclone at station.
NEM	Indicates northeast moving cyclone at station.
SEM	Indicates southeast moving cyclone at station.
COA	Indicates coastal cyclone at station

Figure A.1 Atmospheric particulate sulfur concentration plotted
every 2 hours (Eastern Daylight Time) at Montague, MA
(Site # 1) from September 24 through 30, 1977.

Figure A.2   Atmospheric particulate sulfur concentration plotted every 2 hours (Eastern Daylight Time) at Montague, MA (Site # 1) from October 1 through 7, 1977.

Figure A.3   Atmospheric particulate sulfur concentration plotted every 2 hours (Eastern Daylight Time) at Montague, MA (Site # 1) from October 8 through 14, 1977.

Figure A.4 Atmospheric particulate sulfur concentration plotted every 2 hours (Eastern Daylight Time) at Montague, MA (Site # 1) from October 15 through 21, 1977.
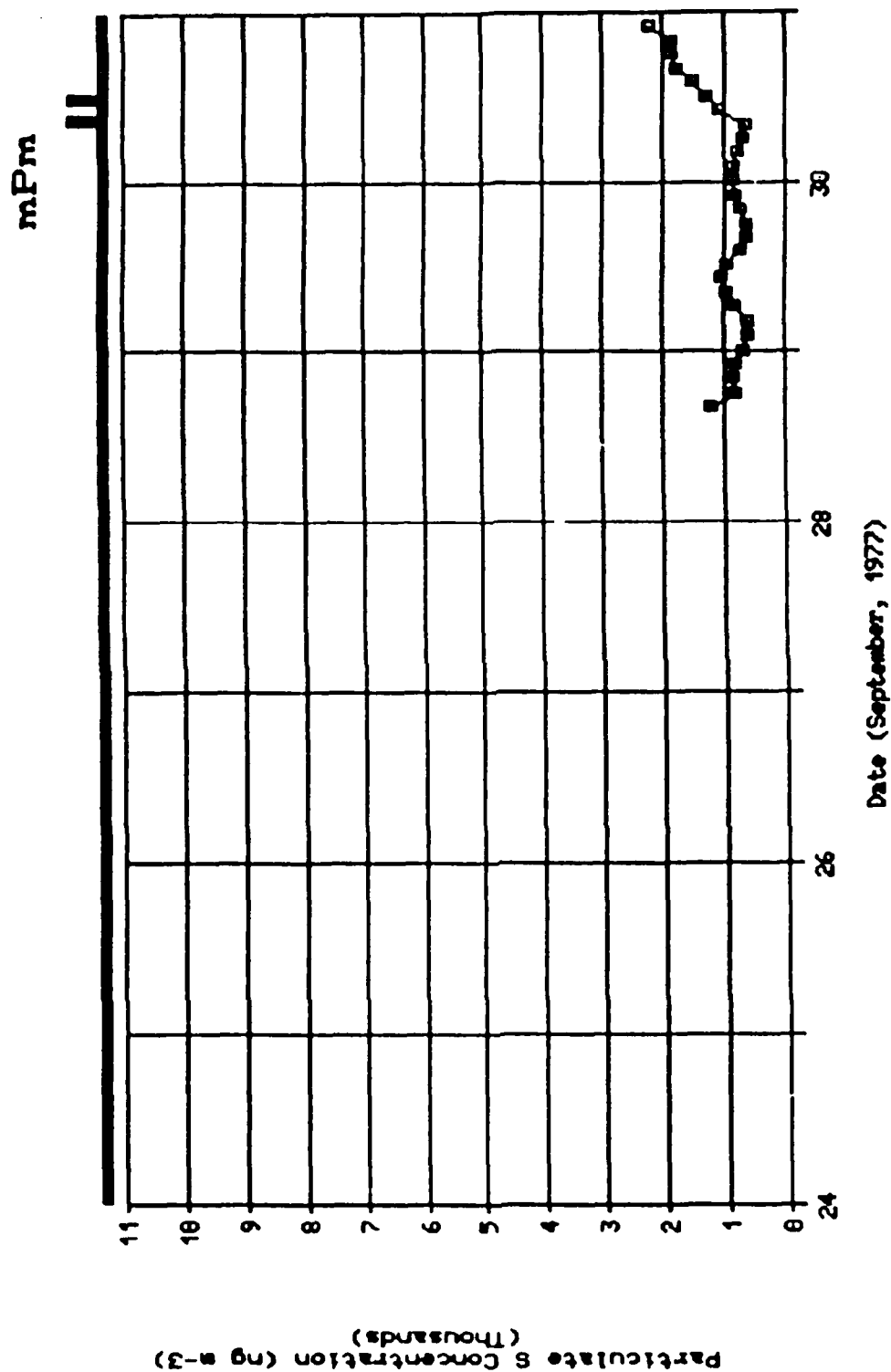
Figure A.5 Atmospheric particulate sulfur concentration plotted every 2 hours (Eastern Daylight Time) at Montague, MA (Site # 1) from October 22 through 28, 1977.
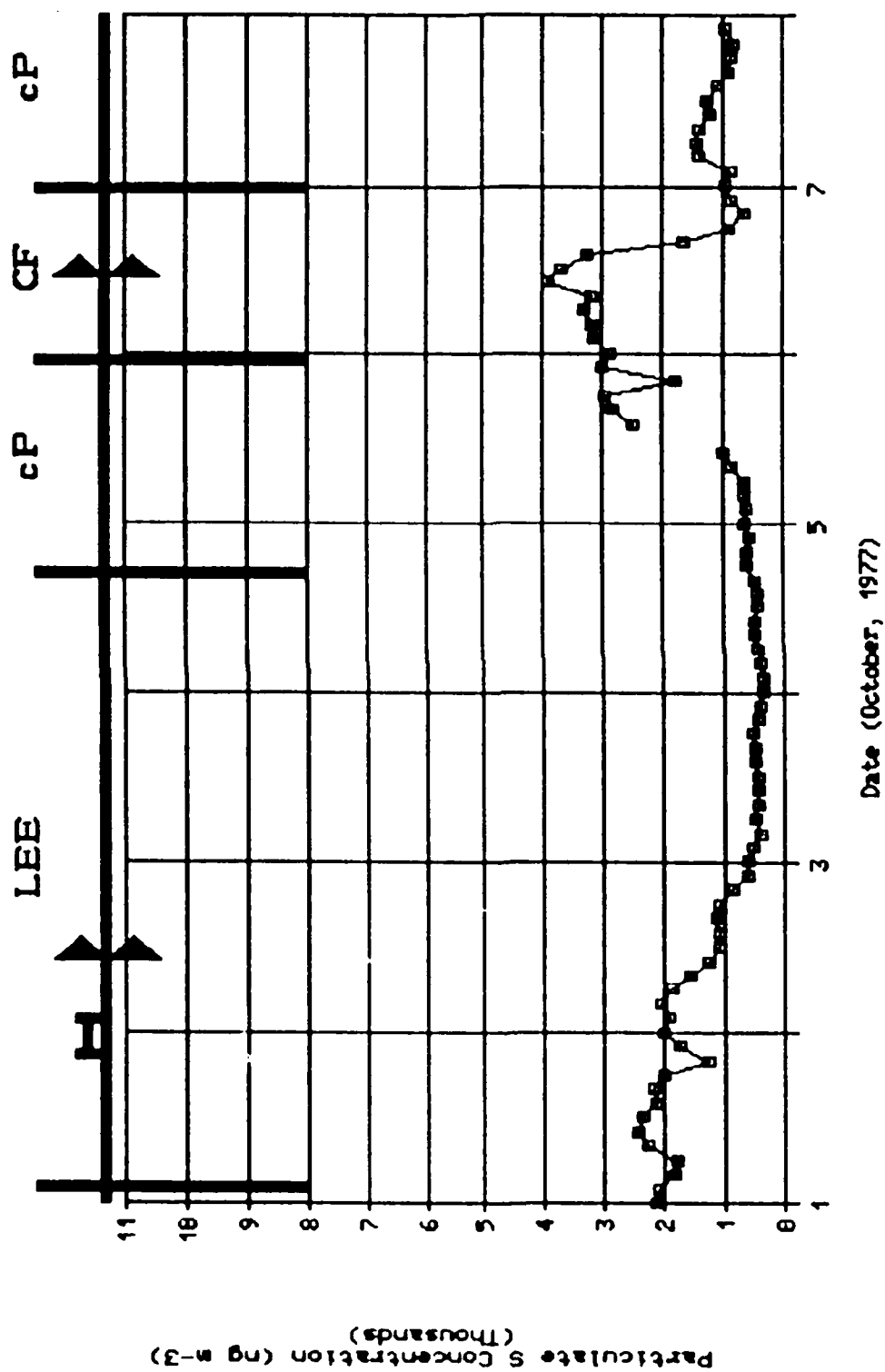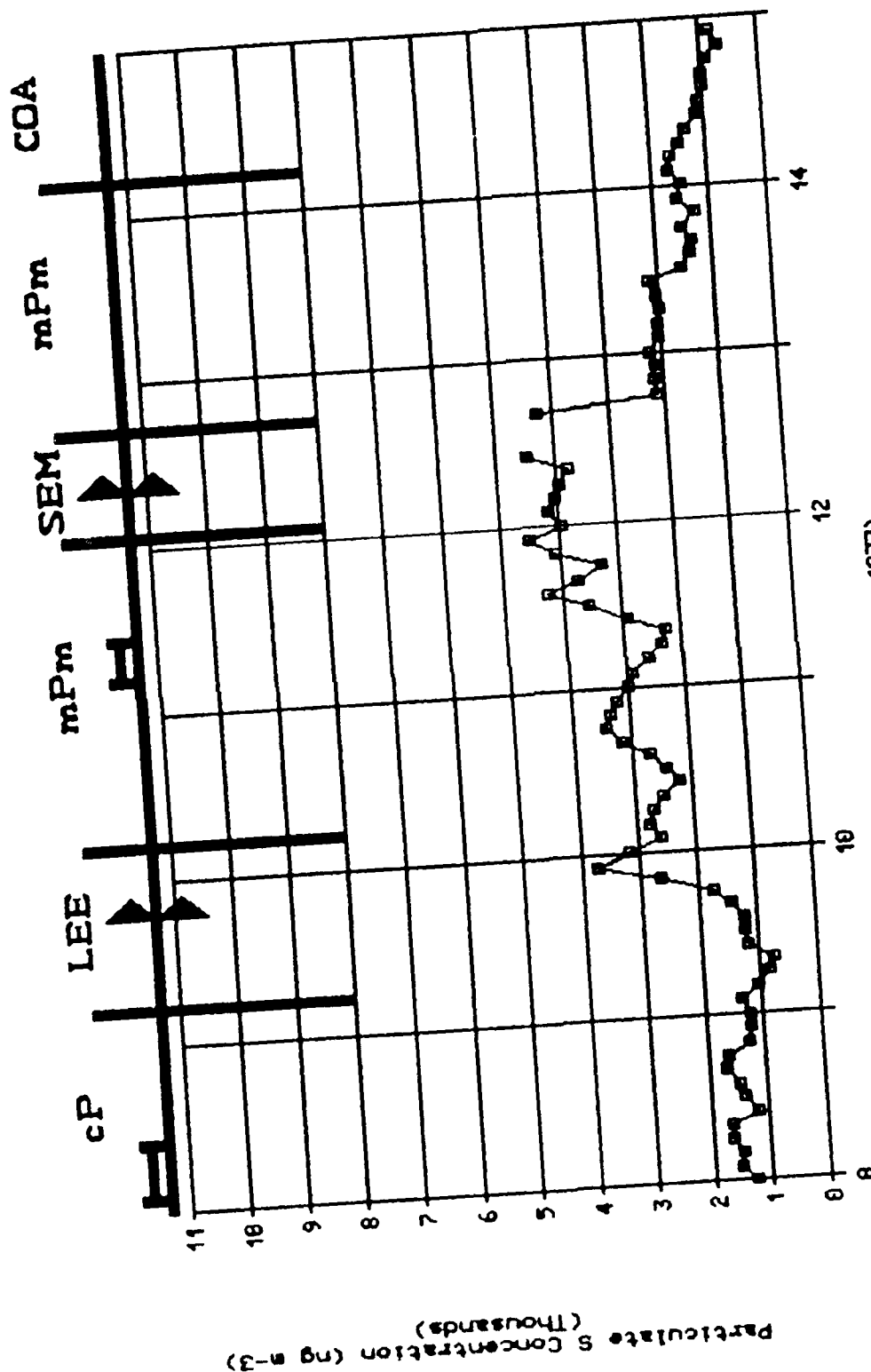
Figure A.6 Atmospheric particulate sulfur concentration plotted
every 2 hours (Eastern Daylight Time) at Montague, MA
(Site # 1) from October 29 through November 4, 1977.

mPm

Date (September, 1977)

Particulate S Concentration (ng m-3)
(Thousands)

11 10 9 8 7 6 5 4 3 2 1 0

24 26 28 30

Figure A.7 Atmospheric particulate sulfur concentration plotted
every 2 hours (Eastern Daylight Time) at Scranton, PA
(Site # 2) from September 24 through 30, 1977.

Figure A.8   Atmospheric particulate sulfur concentration plotted
every 2 hours (Eastern Daylight Time) at Scranton, PA
(Site # 2) from October 1 through 7, 1977.

Figure A.9 Atmospheric particulate sulfur concentration plotted
every 2 hours (Eastern Daylight Time) at Scranton, PA
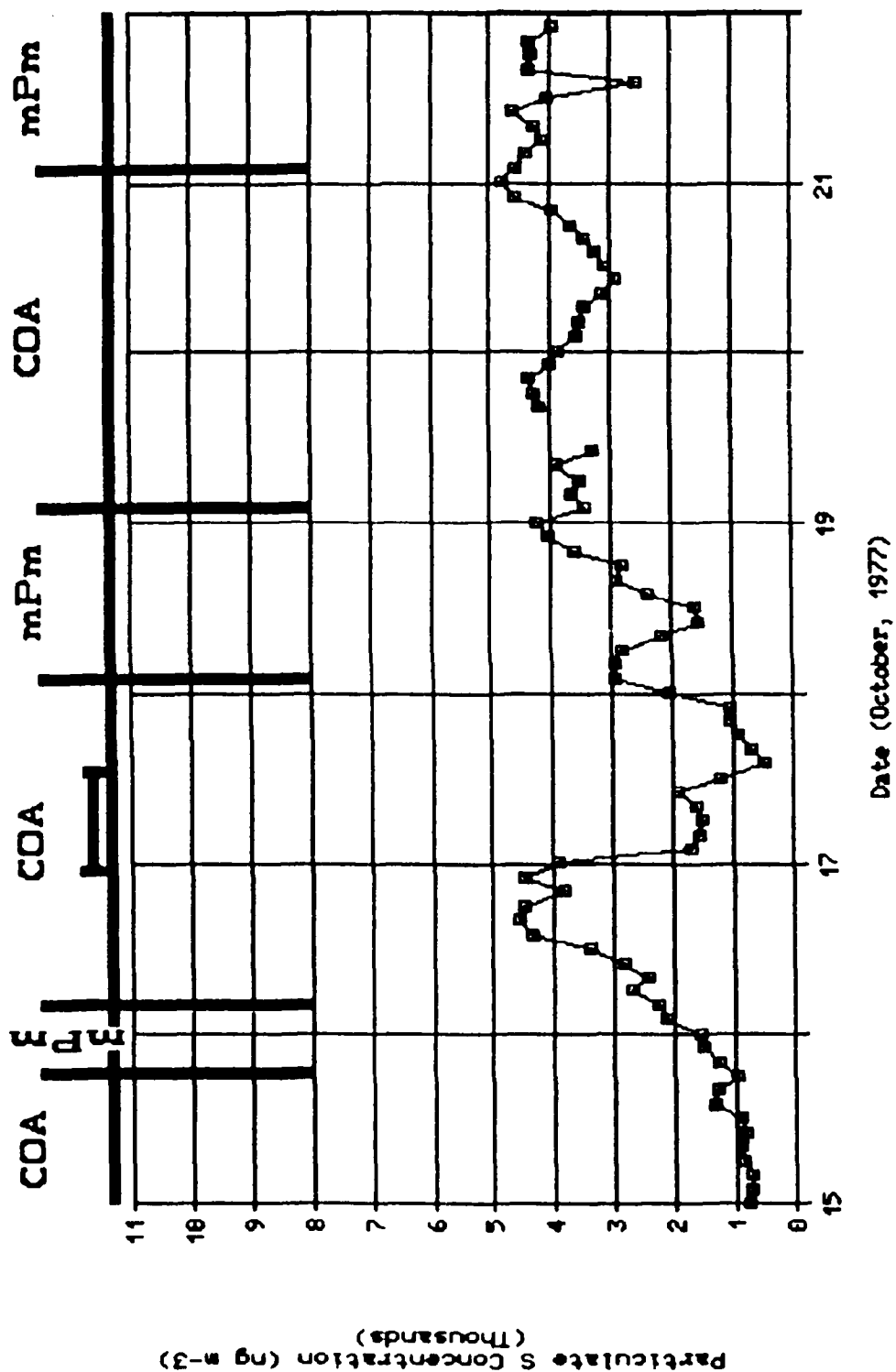(Site # 2) from October 8 through 14, 1977.

Figure A.10 Atmospheric particulate sulfur concentration plotted every 2 hours (Eastern Daylight Time) at Scranton, PA (Site # 2) from October 15 through 21, 1977.
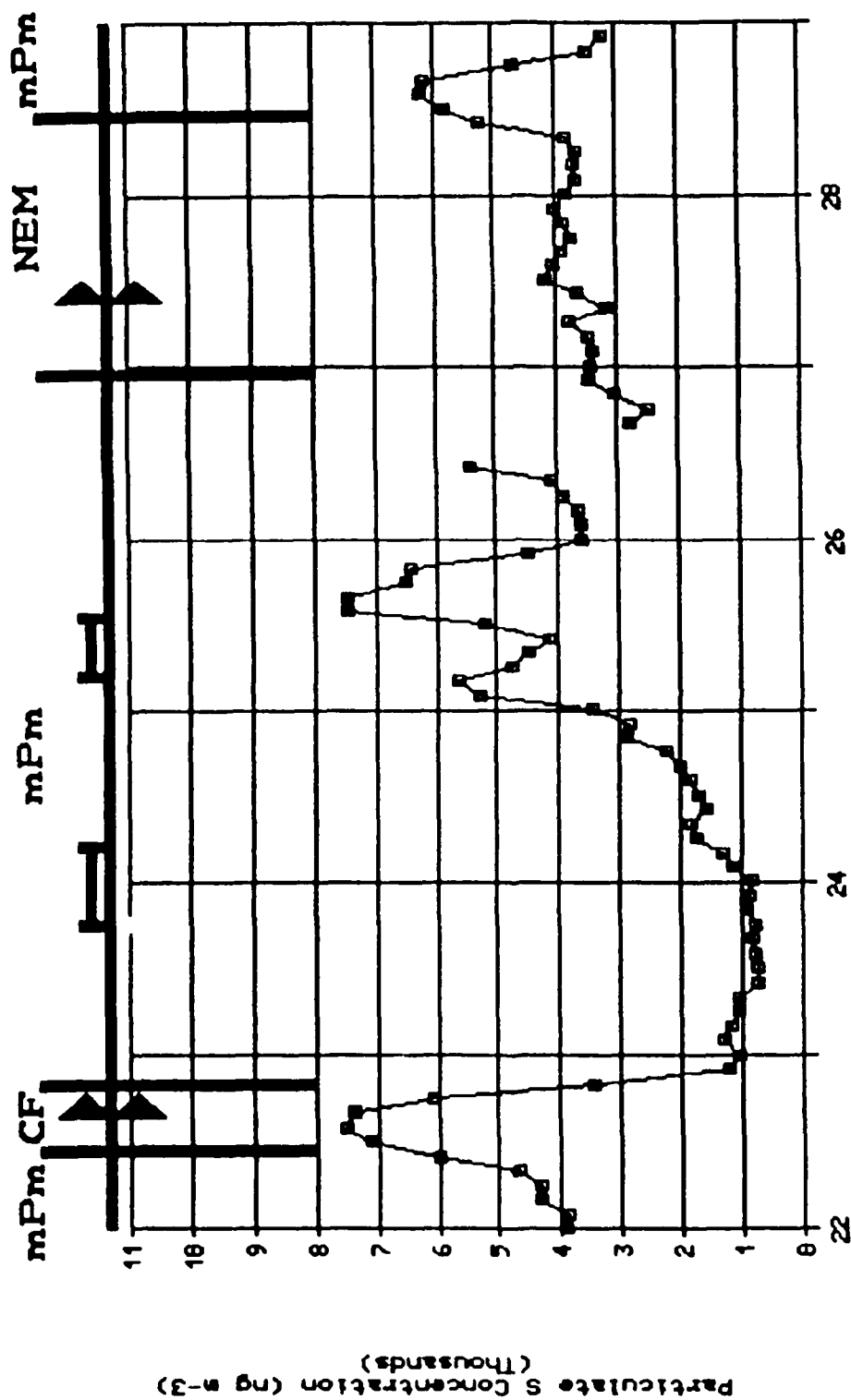
Figure A.11 Atmospheric particulate sulfur concentration plotted
every 2 hours (Eastern Daylight Time) at Scranton, PA
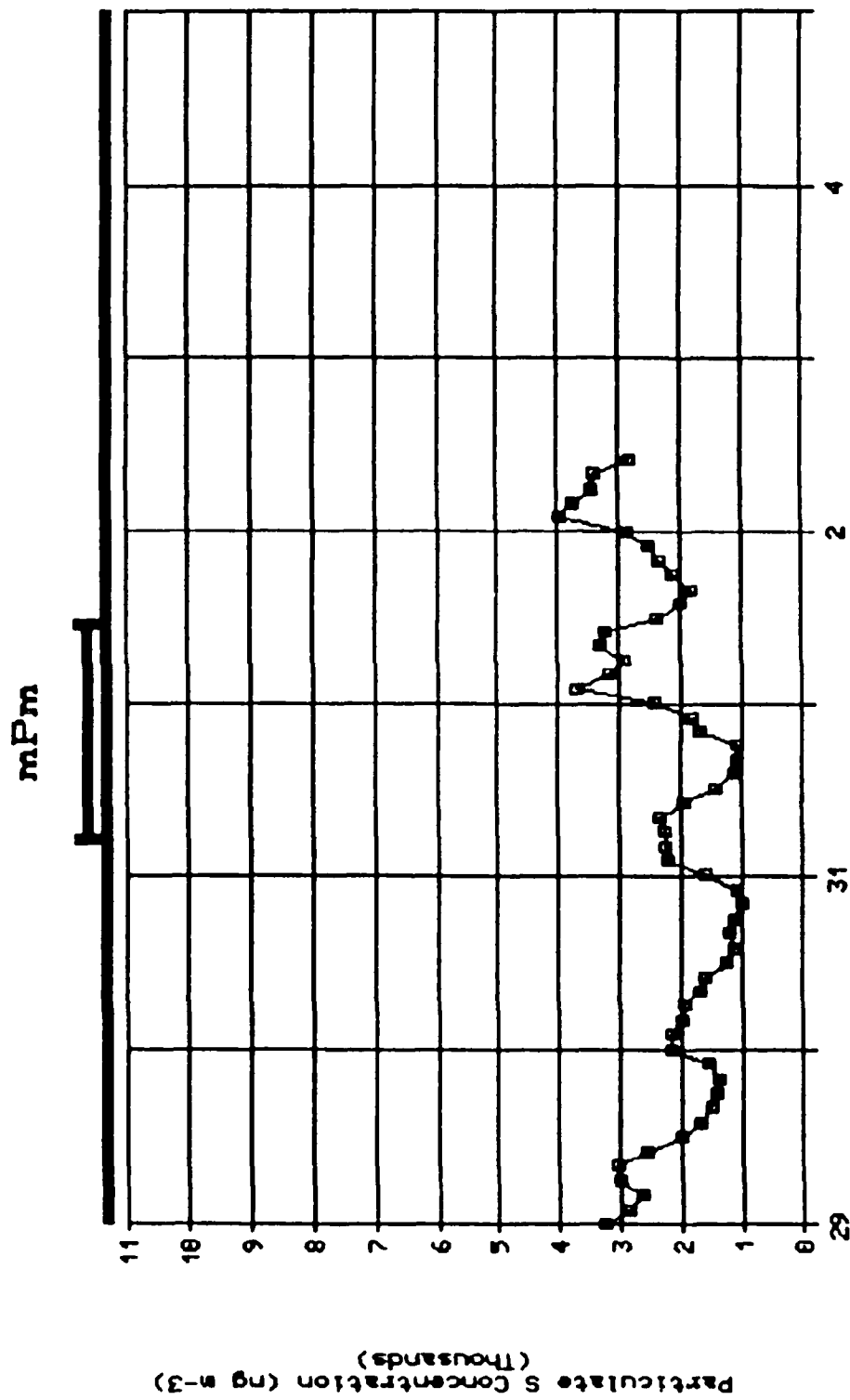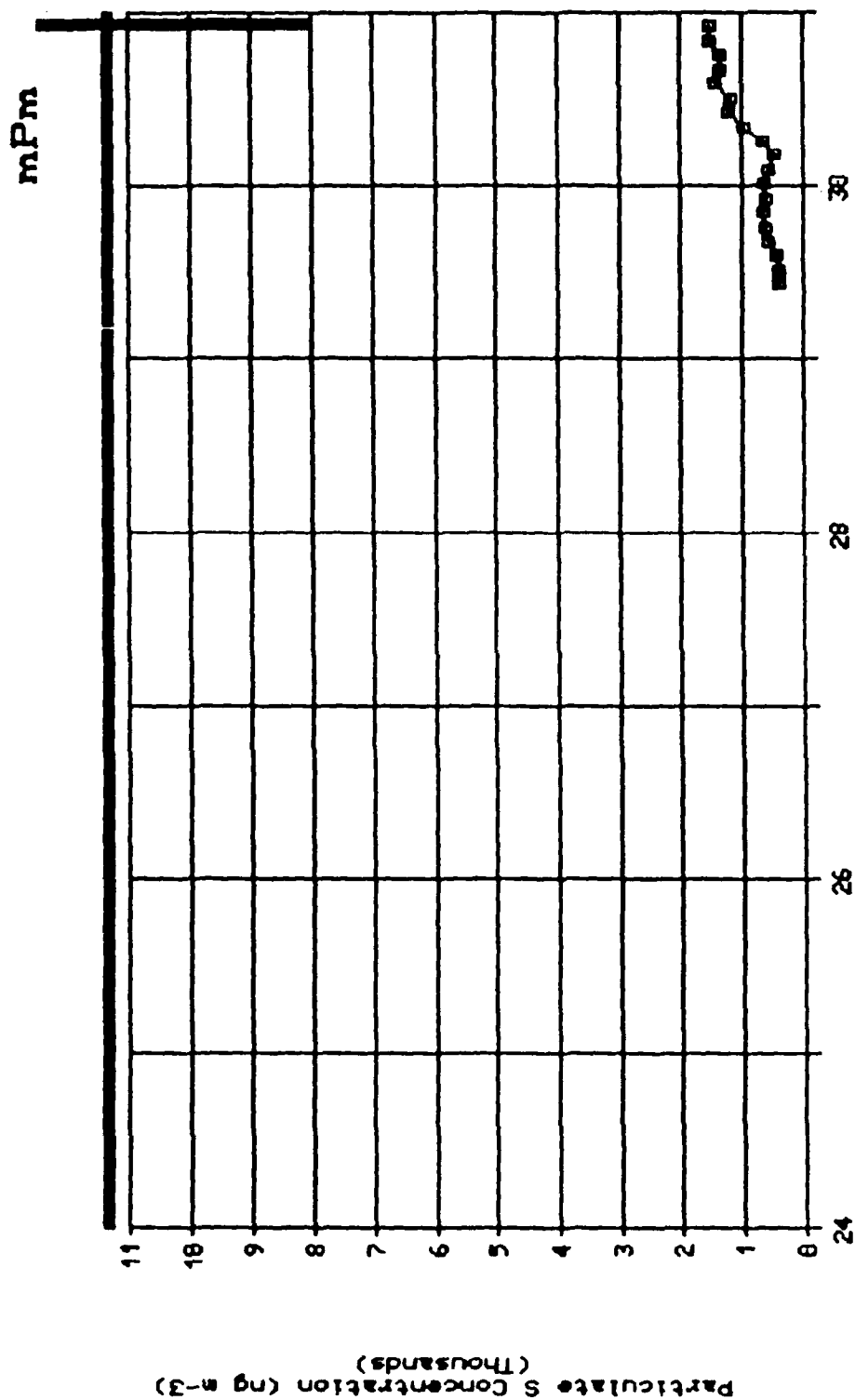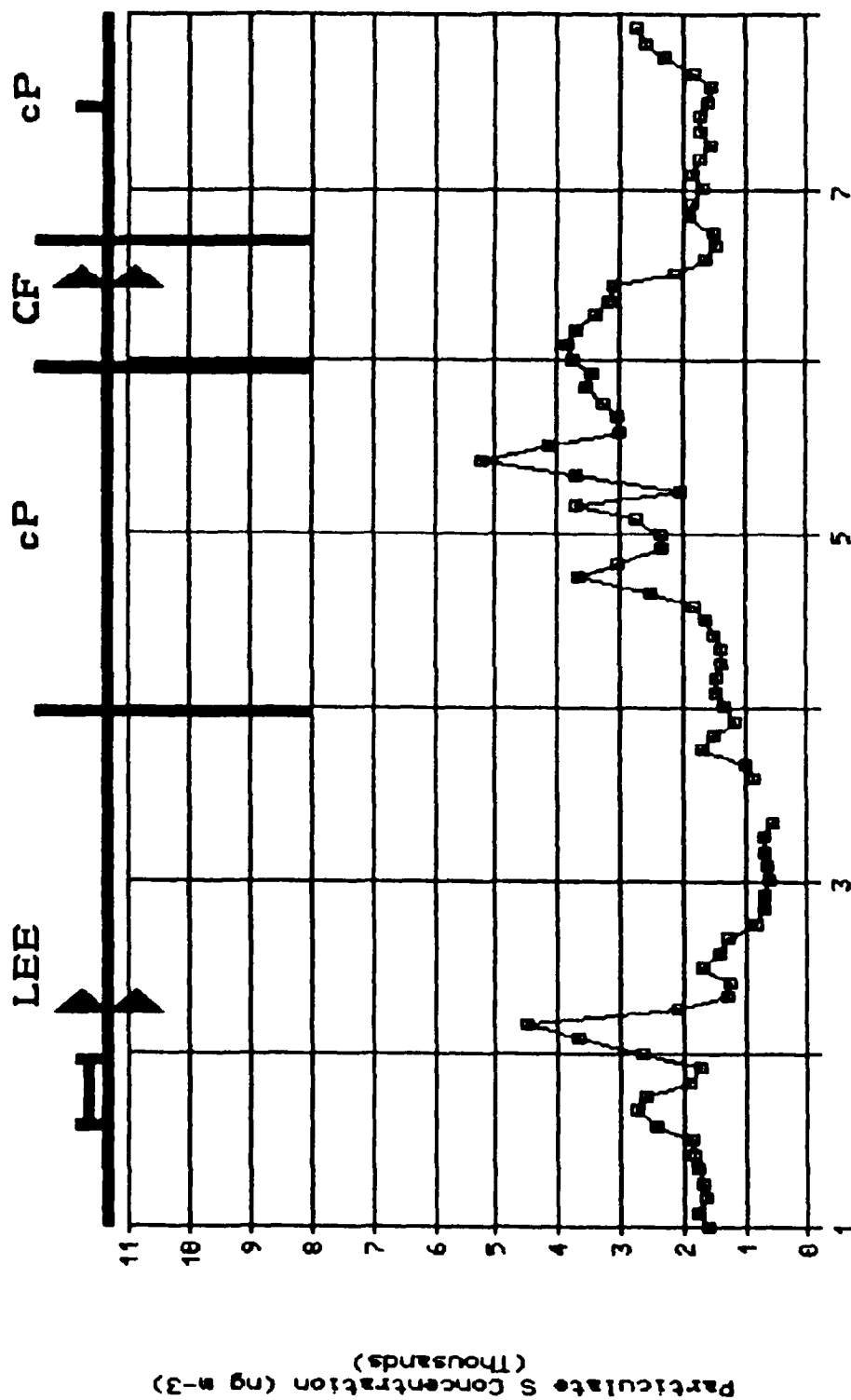(Site # 2) from October 22 through 28, 1977.

Figure A.12 Atmospheric particulate sulfur concentration plotted every 2 hours (Eastern Daylight Time) at Scranton, PA (Site # 2) from October 29 through November 4, 1977.

mPm

Particulate S Concentration (ng m-3)
(Thousands)

Date (September, 1977)

Figure A.13 Atmospheric particulate sulfur concentration plotted
every 2 hours (Eastern Daylight Time) at Indian River,
DE (Site # 3) from September 24 through 30, 1977.

Figure A.14 Atmospheric particulate sulfur concentration plotted every 2 hours (Eastern Daylight Time) at Indian River, DE (Site # 3) from October 1 through 7, 1977.

Figure A.15 Atmospheric particulate sulfur concentration plotted every 2 hours (Eastern Daylight Time) at Indian River, DE (Site # 3) from October 8 through 14, 1977.
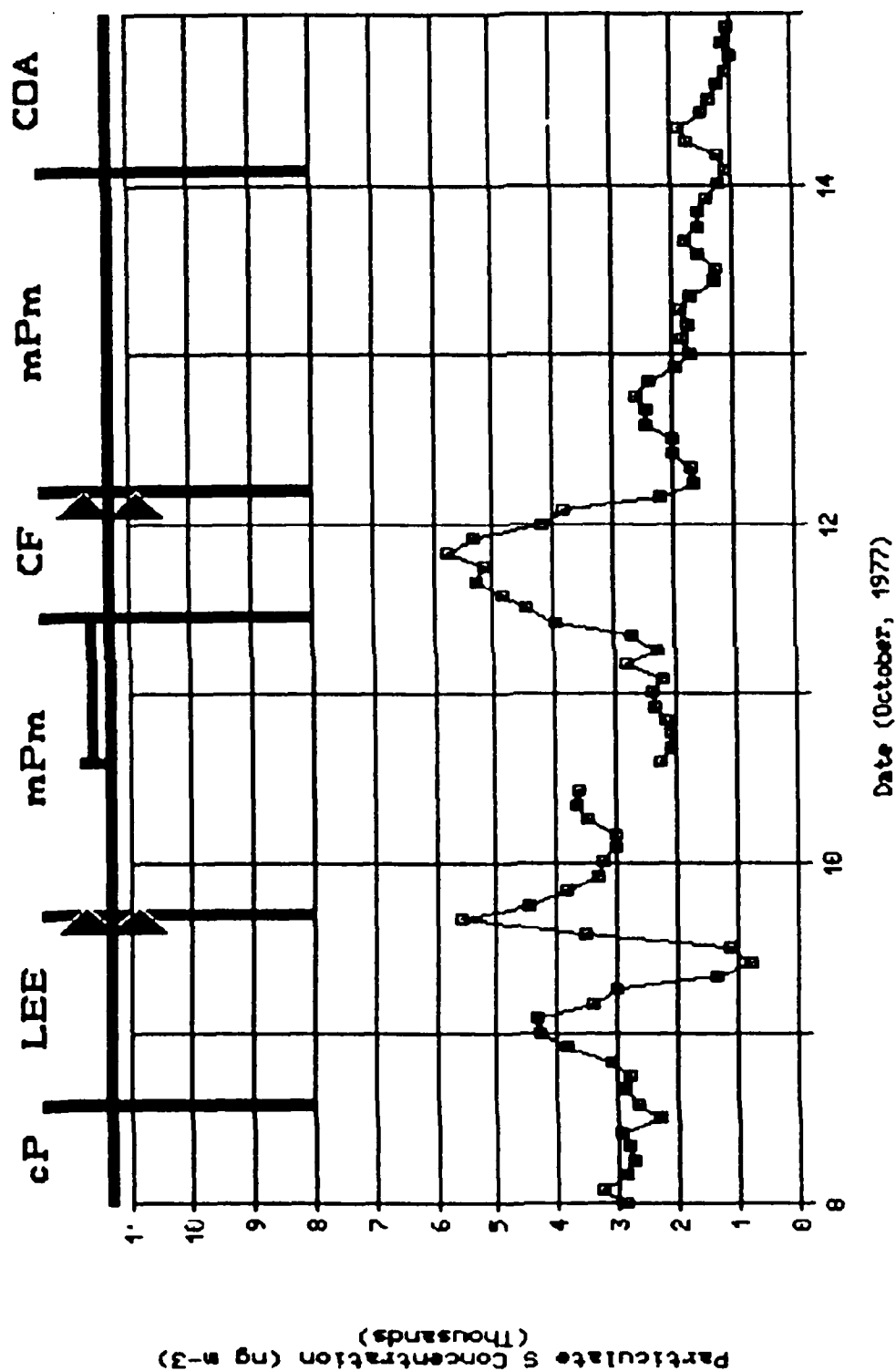
Figure A.16 Atmospheric particulate sulfur concentration plotted every 2 hours (Eastern Daylight Time) at Indian River, DE (Site # 3) from October 15 through 21, 1977.

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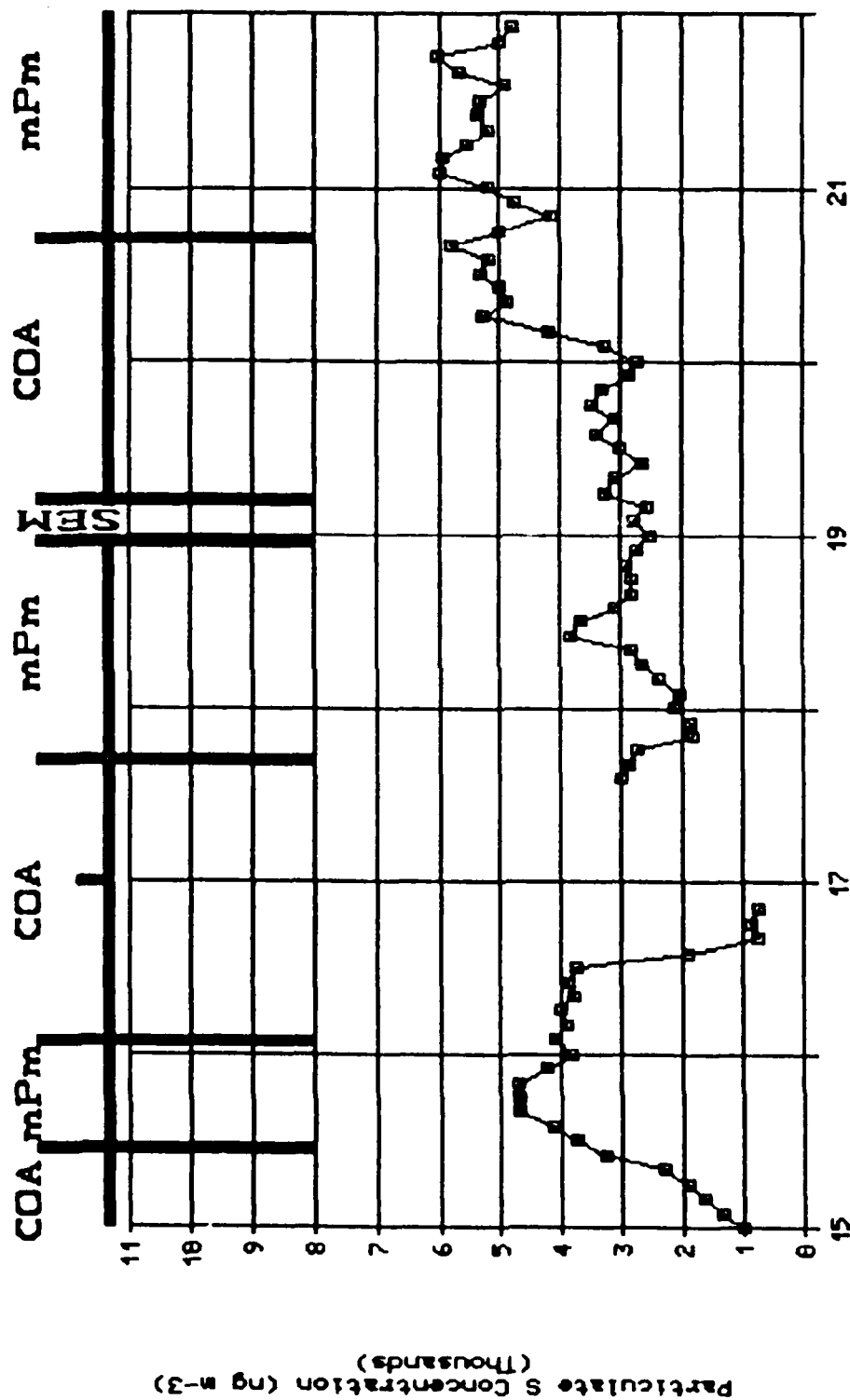

Figure A.17 Atmospheric particulate sulfur concentration plotted every 2 hours (Eastern Daylight Time) at Indian River, DE (Site # 3) from October 22 through 28, 1977.

Figure A.18 Atmospheric particulate sulfur concentration plotted every 2 hours (Eastern Daylight Time) at Indian River, DE (Site # 5) from October 29 through November 4, 1977.

Figure A.19 Atmospheric particulate sulfur concentration plotted every 2 hours (Eastern Daylight Time) at Duncan Falls, OH (Site # 4) from September 24 through 30, 1977.

Figure A.20 Atmospheric particulate sulfur concentration plotted every 2 hours (Eastern Daylight Time) at Duncan Falls, OH (Site # 4) from October 1 through 7, 1977.
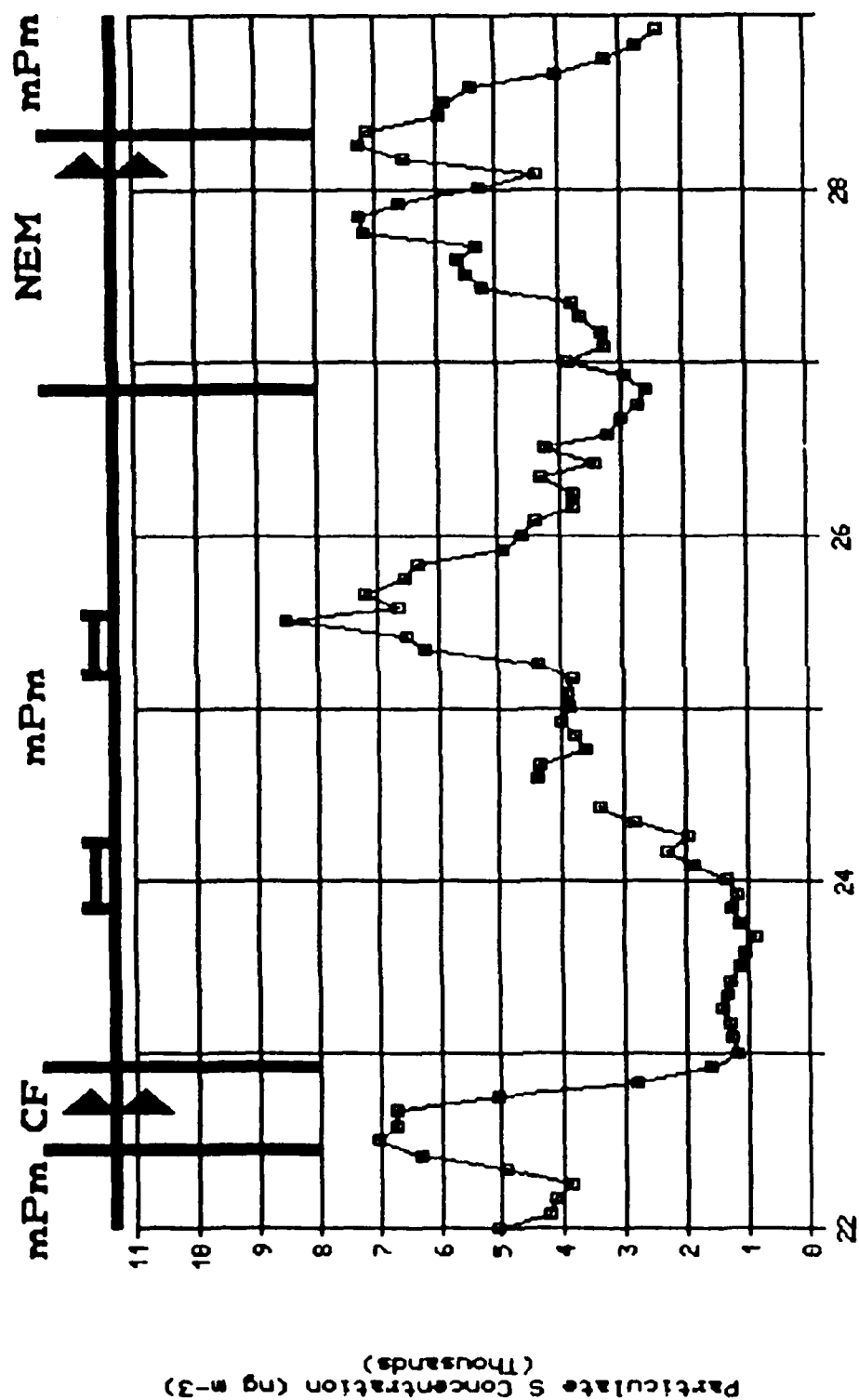
Figure A.21 Atmospheric particulate sulfur concentration plotted
every 2 hours (Eastern Daylight Time) at Duncan Falls,
OH (Site # 4) from October 8 through 14, 1977.

Figure A.22 Atmospheric particulate sulfur concentration plotted every 2 hours (Eastern Daylight Time) at Duncan Falls, OH (Site # 4) from October 15 through 21, 1977.

Figure A.23 Atmospheric particulate sulfur concentration plotted
every 2 hours (Eastern Daylight Time) at Duncan Falls,
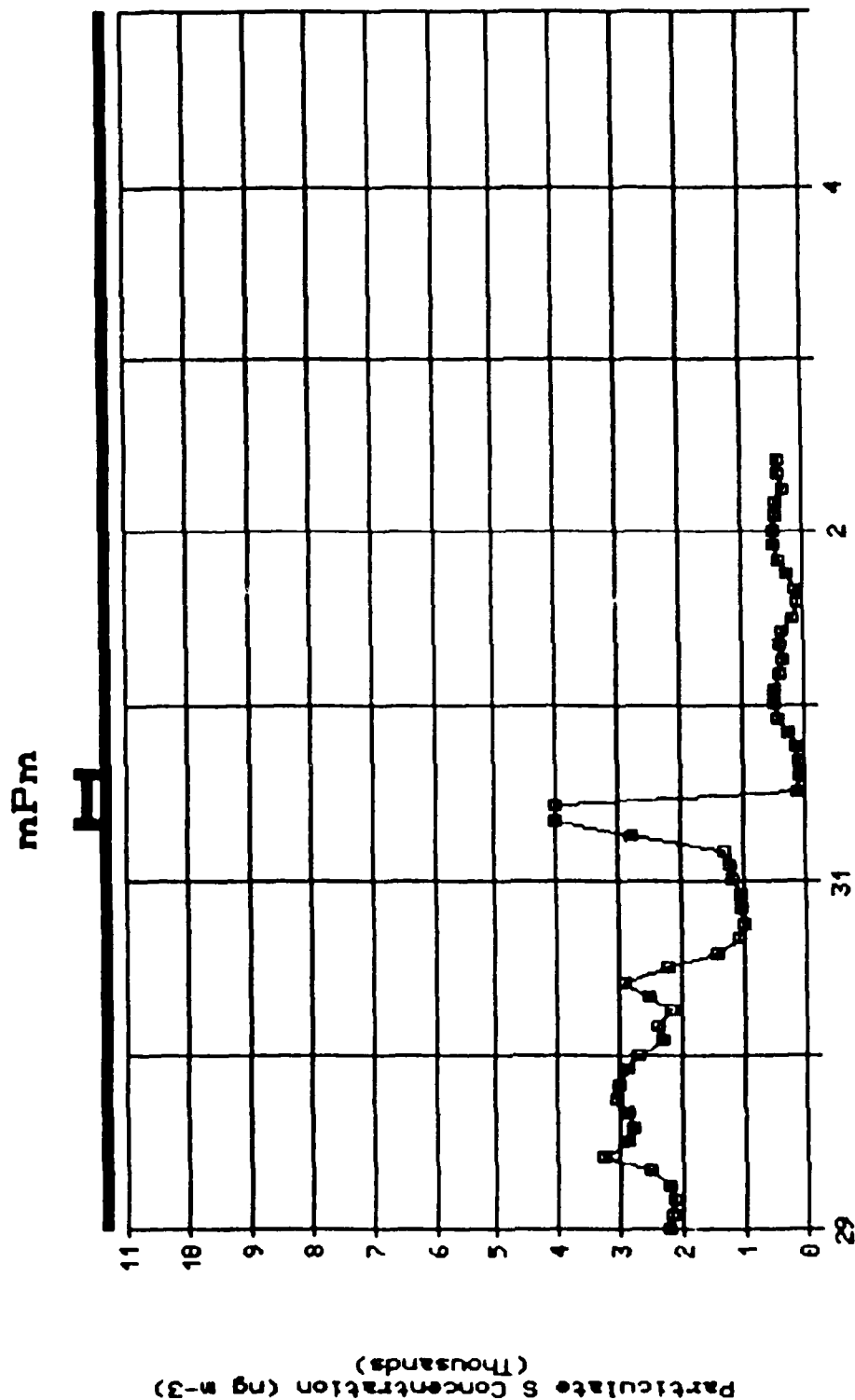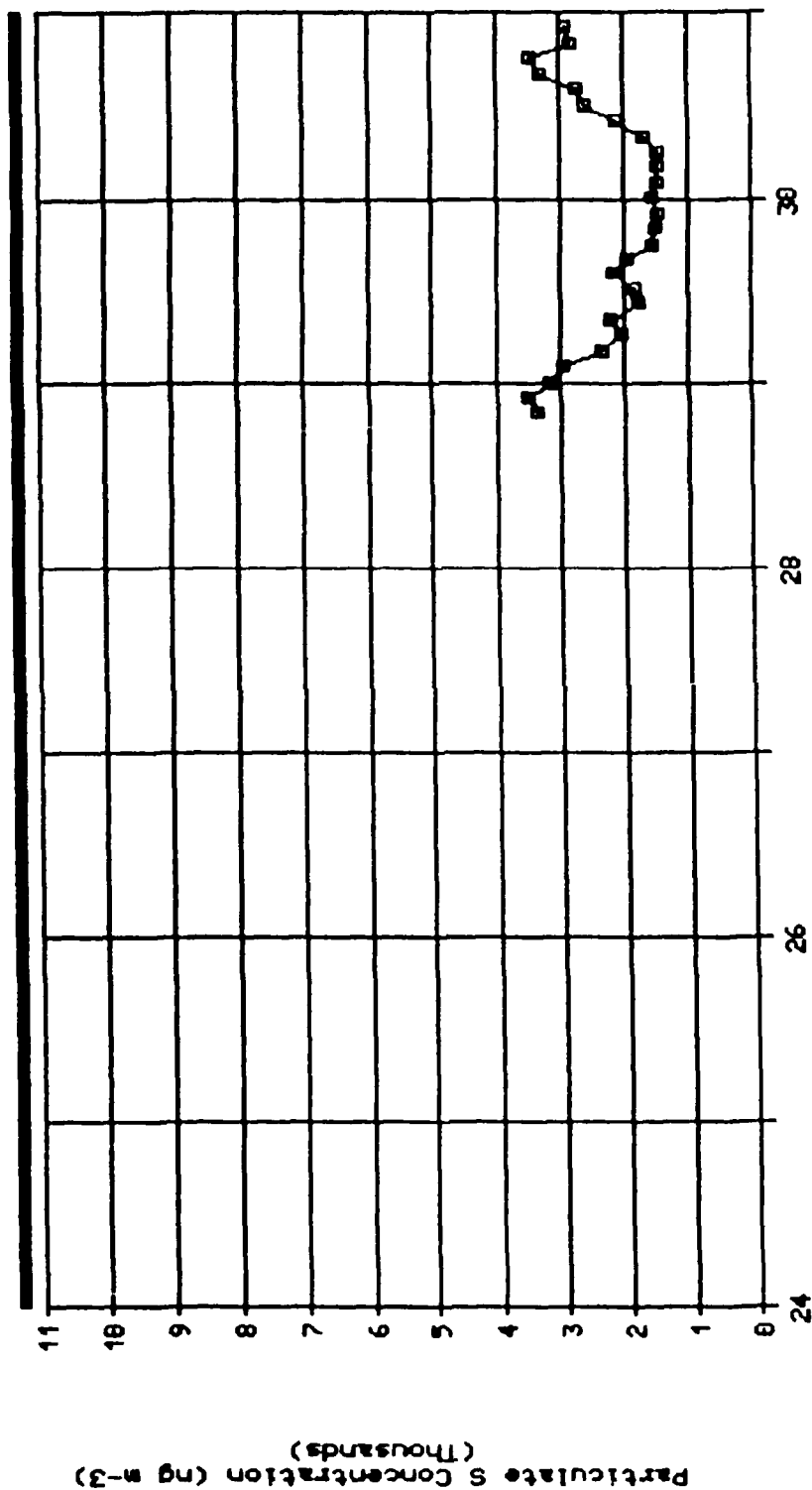OH (Site # 4) from October 22 through 28, 1977.

mPm

Figure A.24 Atmospheric particulate sulfur concentration plotted
every 2 hours (Eastern Daylight Time) at Duncan Falls,
OH (Site # 4) from October 29 through November 4, 1977.

Figure A.25 Atmospheric particulate sulfur concentration plotted
every 2 hours (Eastern Daylight Time) at Rockport, IN
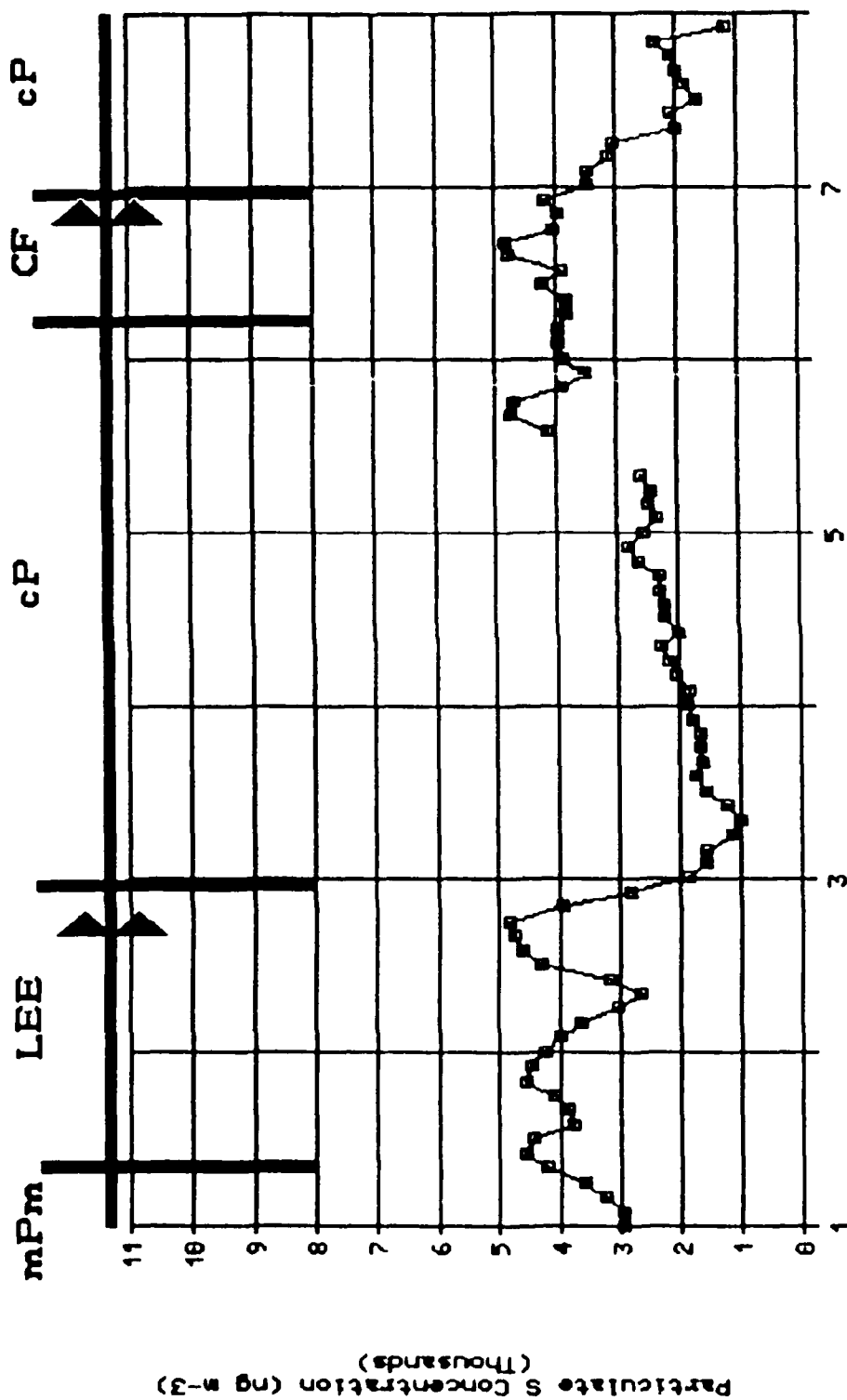(Site # 5) from September 24 through 30, 1977.

Figure A.26 Atmospheric particulate sulfur concentration plotted
every 2 hours (Eastern Daylight Time) at Rockport, IN
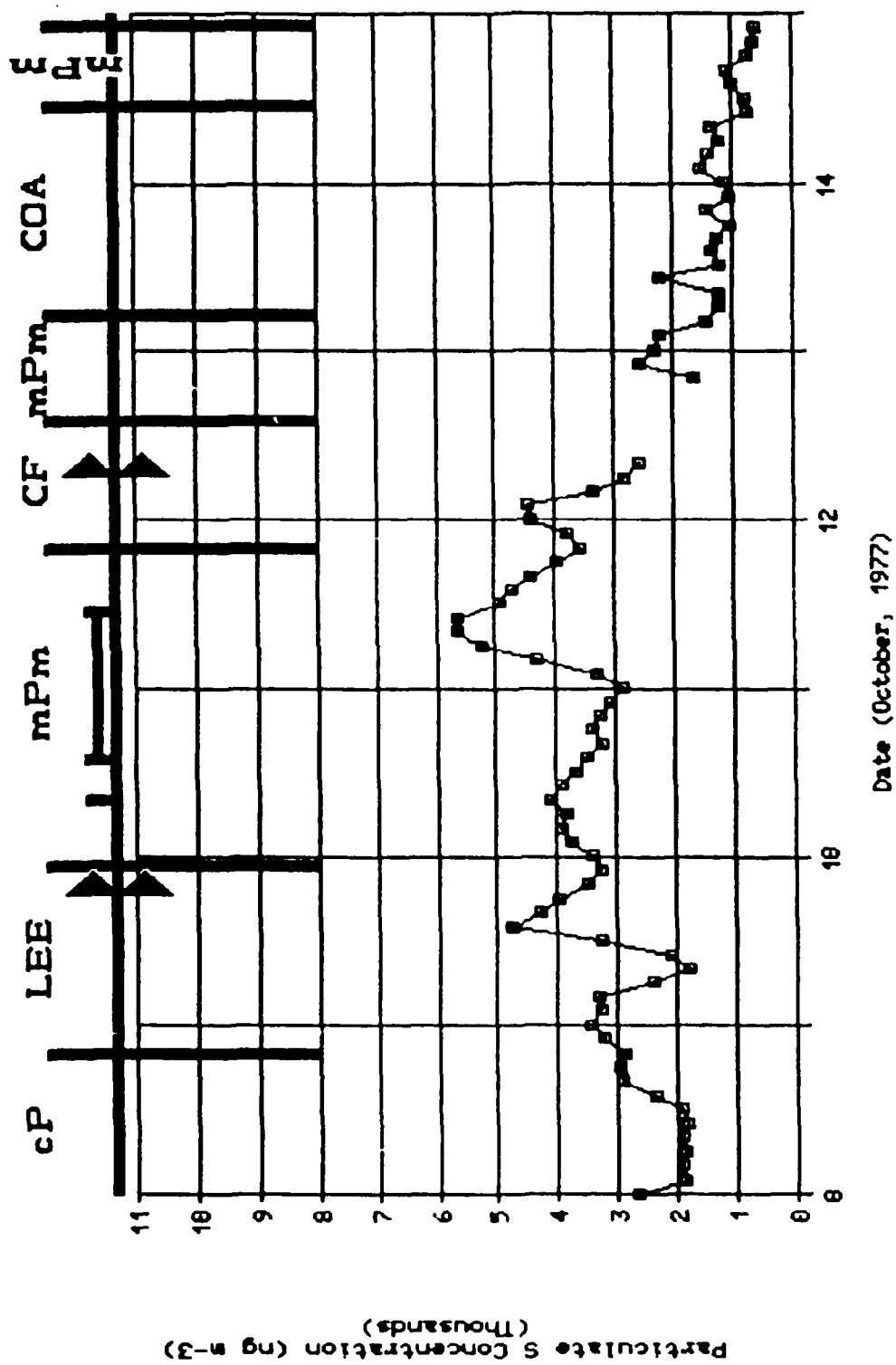(Site # 5) from October 1 through 7, 1977.

Figure A.27 Atmospheric particulate sulfur concentration plotted
every 2 hours (Eastern Daylight Time) at Rockport, IN
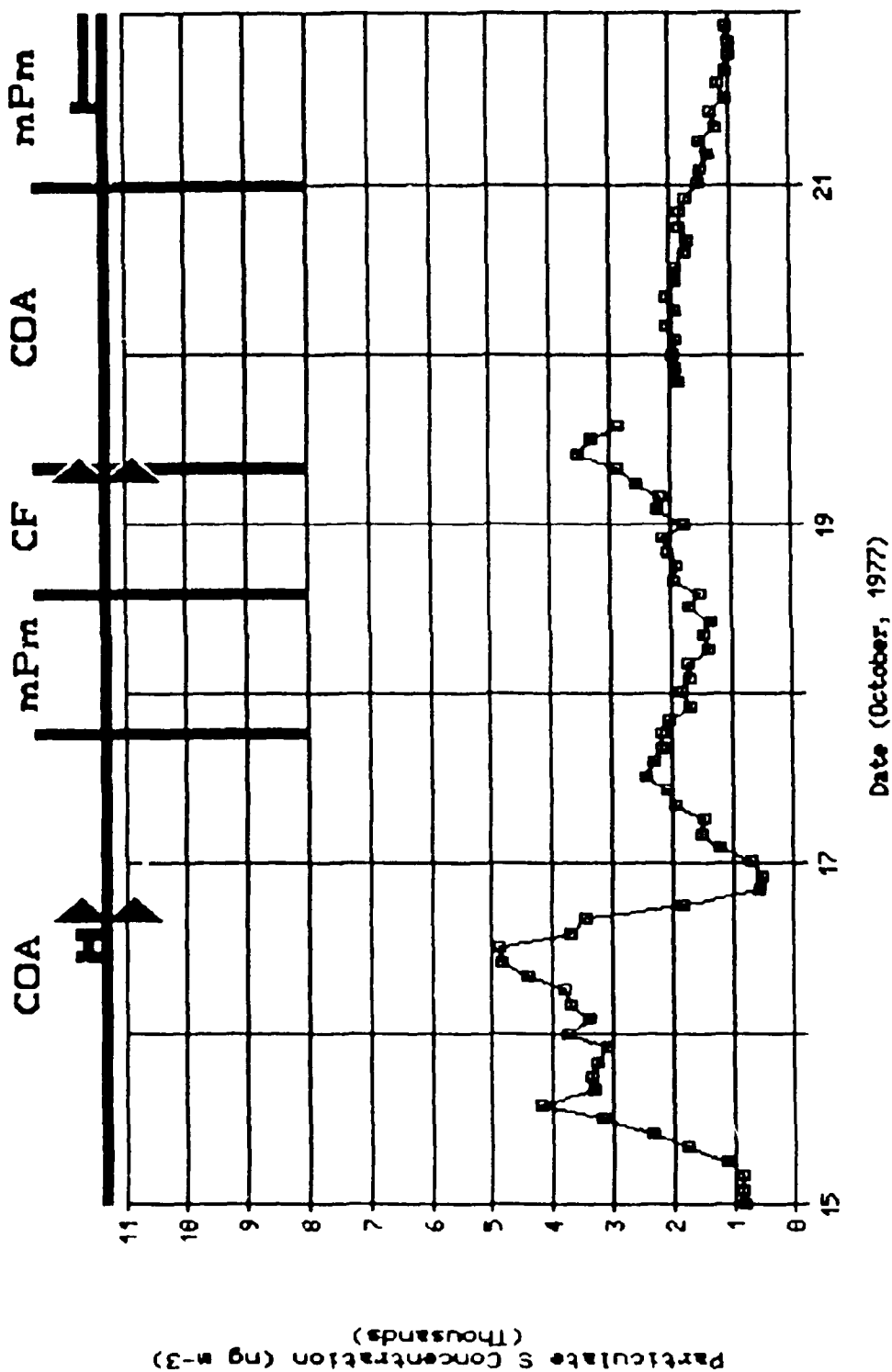(Site # 5) from October 8 through 14, 1977.

Figure A.28 Atmospheric particulate sulfur concentration plotted every 2 hours (Eastern Daylight Time) at Rockport, IN (Site # 5) from October 15 through 21, 1977.

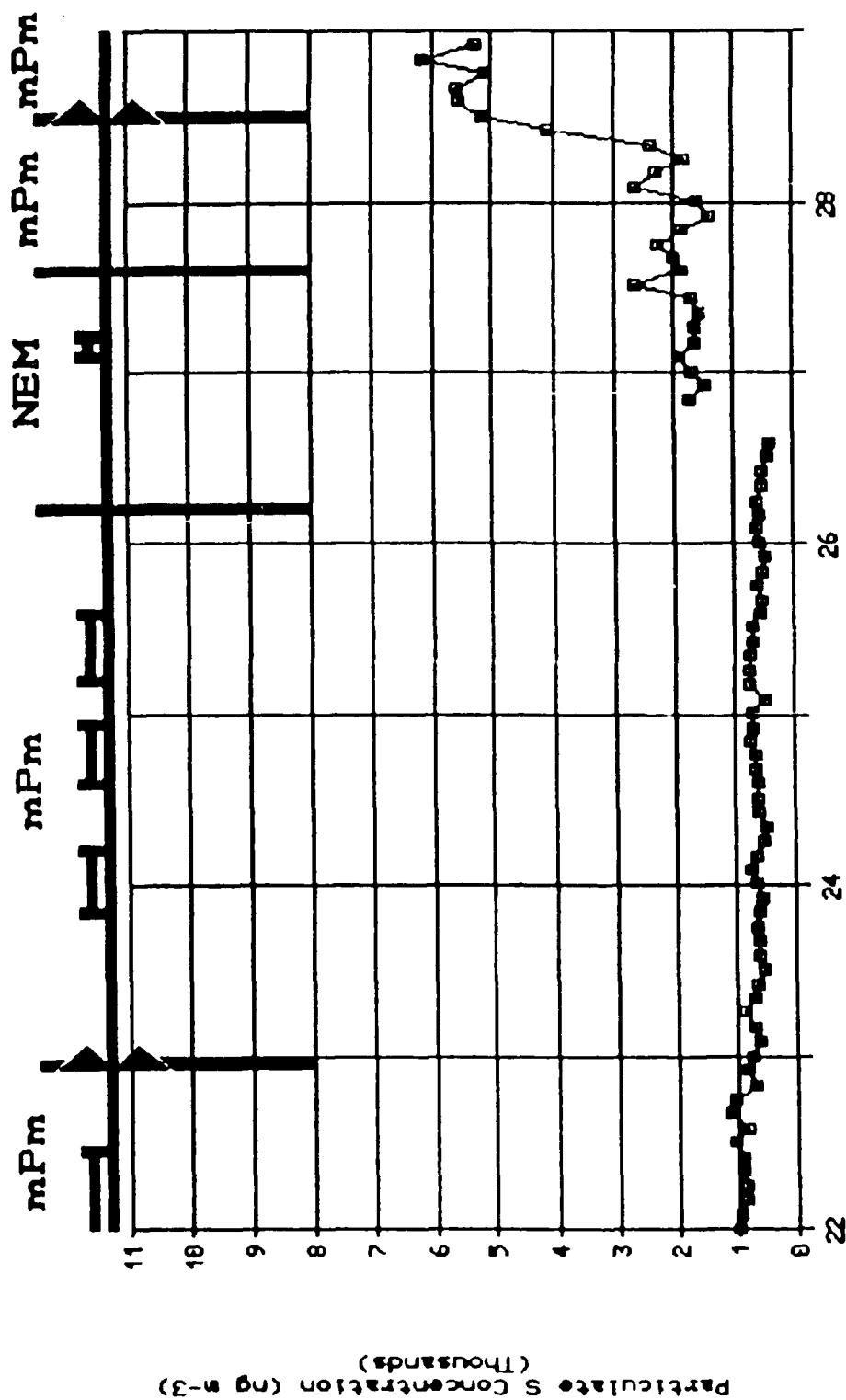Figure A.29 Atmospheric particulate sulfur concentration plotted every 2 hours (Eastern Daylight Time) at Rockport, IN (Site # 5) from October 22 through 28, 1977.

LEE

mPm

Particulate S Concentration (ng m-3)
(Thousands)

Date (29 October - 4 November, 1977)

Figure A.30 Atmospheric particulate sulfur concentration plotted
every 2 hours (Eastern Daylight Time) at Rockport, IN
(Site # 5) from October 29 through November 4, 1977.

Figure A.31 Atmospheric particulate sulfur concentration plotted every 2 hours (Eastern Daylight Time) at Giles County, TN (Site # 6) from September 24 through 30, 1977.

Figure A.32 Atmospheric particulate sulfur concentration plotted every 2 hours (Eastern Daylight Time) at Giles County, TN (Site # 6) from October 1 through 7, 1977.
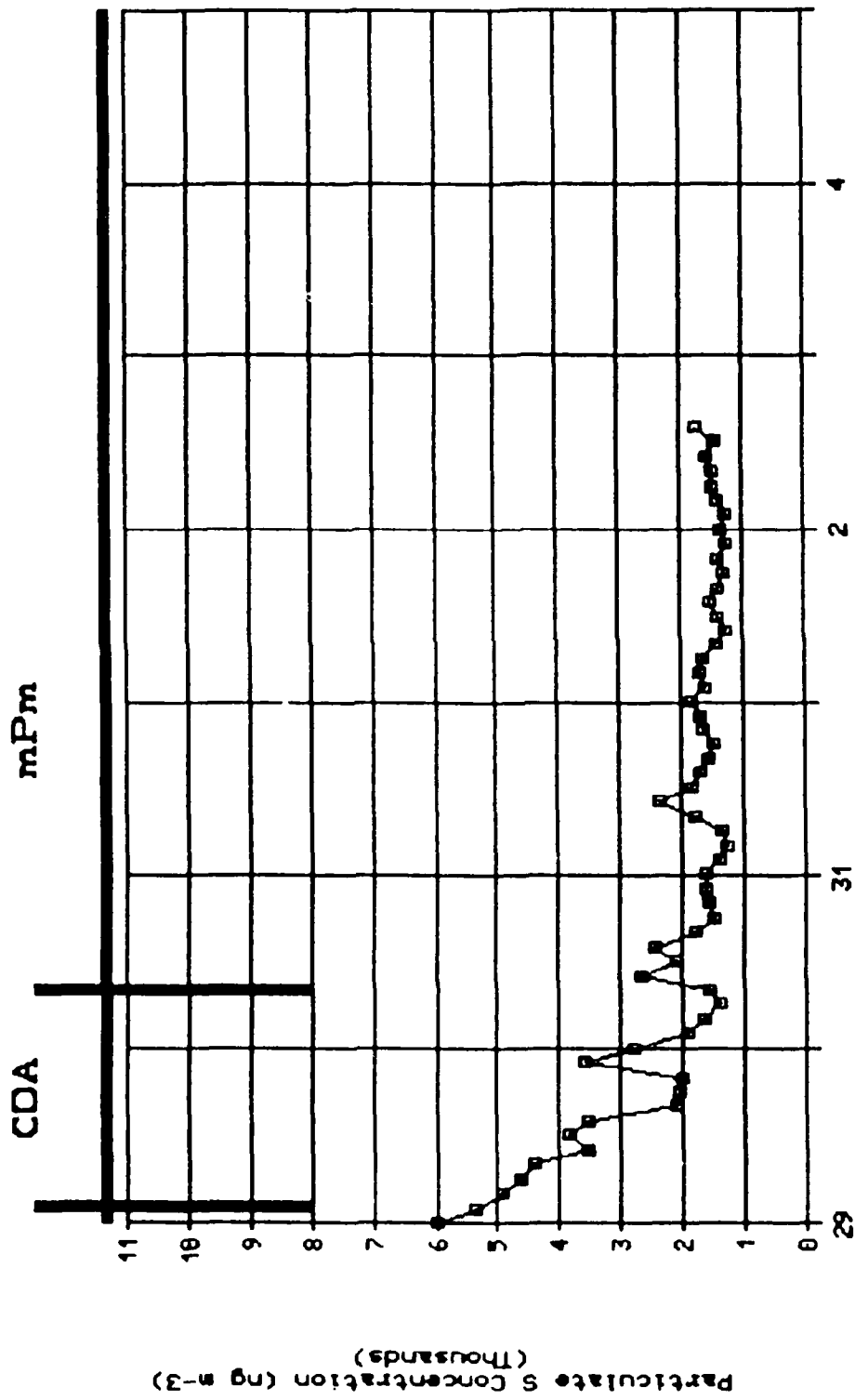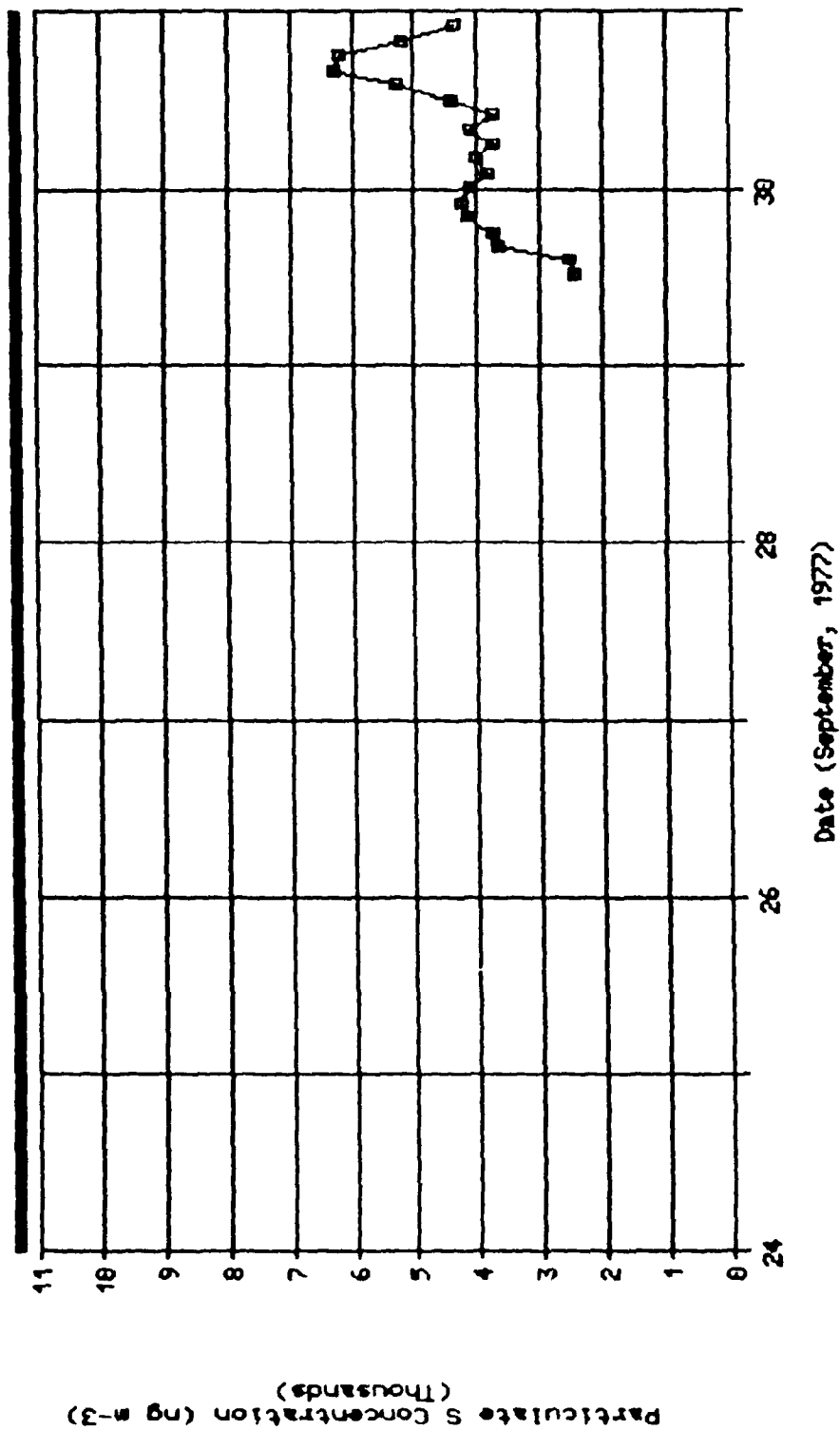
Figure A.33 Atmospheric particulate sulfur concentration plotted every 2 hours (Eastern Daylight Time) at Giles County, TN (Site # 6) from October 8 through 14, 1977.

Figure A.34 Atmospheric particulate sulfur concentration plotted
every 2 hours (Eastern Daylight Time) at Giles County,
TN (Site # 6) from October 15 through 21, 1977.
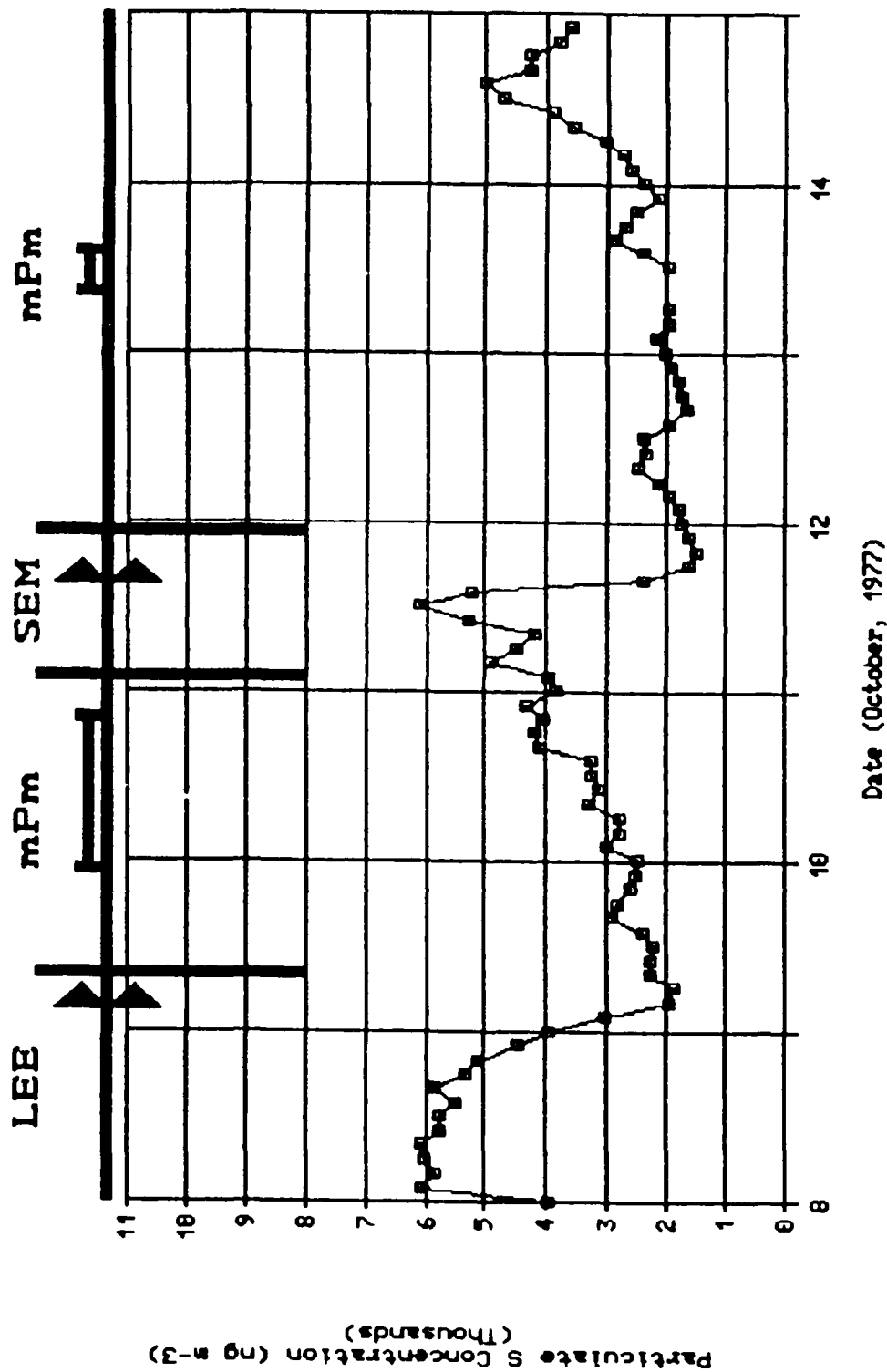
Figure A.35 Atmospheric particulate sulfur concentration plotted
every 2 hours (Eastern Daylight Time) at Giles County,
TN (Site # 6) from October 22 through 28, 1977.

Figure A.36 Atmospheric particulate sulfur concentration plotted
every 2 hours (Eastern Daylight Time) at Giles County,
TN (Site # 6) from October 29 through November 4, 1977.

Figure A.37 Atmospheric particulate sulfur concentration plotted every 2 hours (Eastern Daylight Time) at Ft. Wayne, IN (Site # 7) from September 24 through 30, 1977.
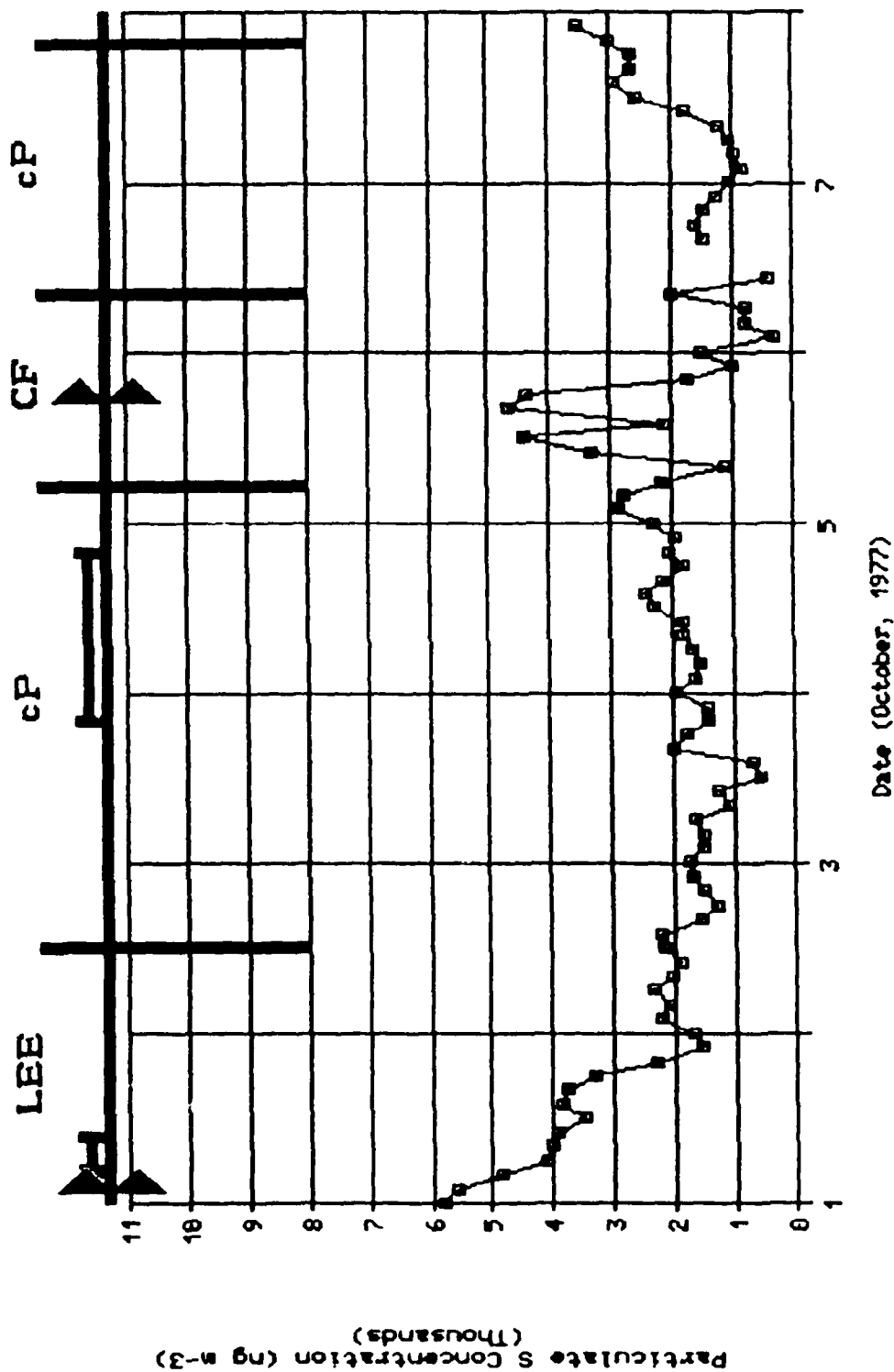
Figure A.38 Atmospheric particulate sulfur concentration plotted
every 2 hours (Eastern Daylight Time) at Ft. Wayne, IN
(Site # 7) from October 1 through 7, 1977.
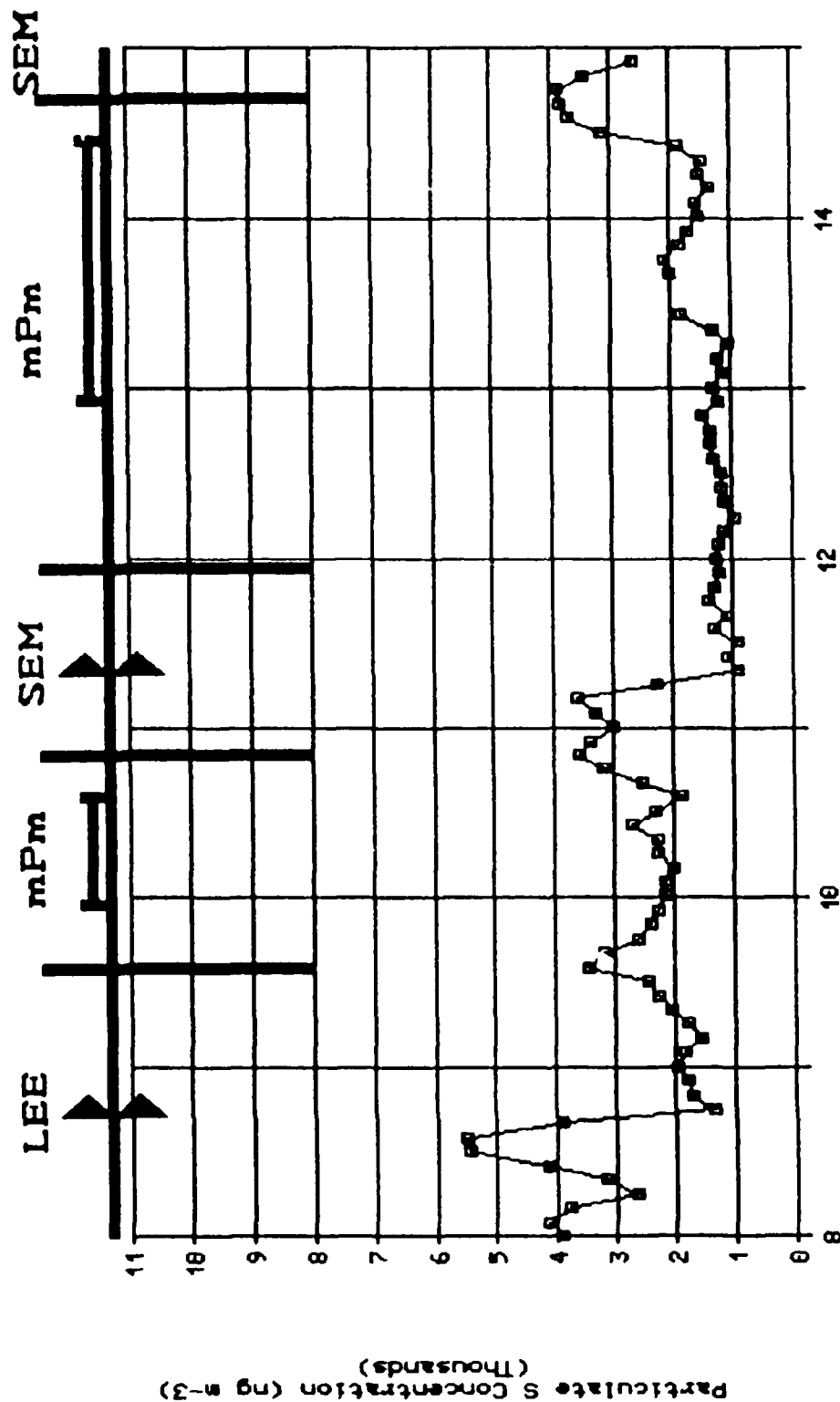
Figure A.39 Atmospheric particulate sulfur concentration plotted
every 2 hours (Eastern Daylight Time) at FT. Wayne, IN
(Site # 7) from October 8 through 14, 1977.
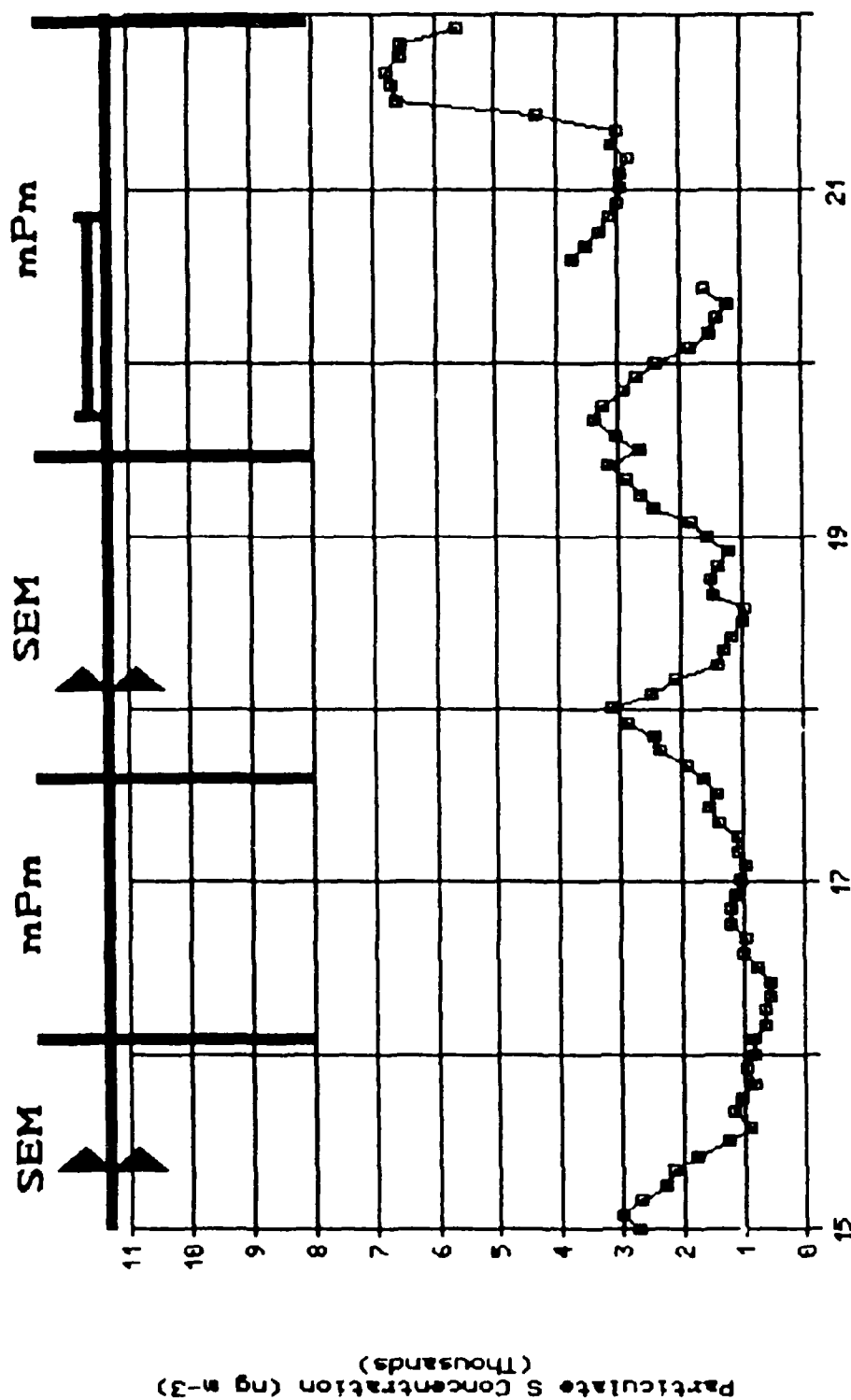
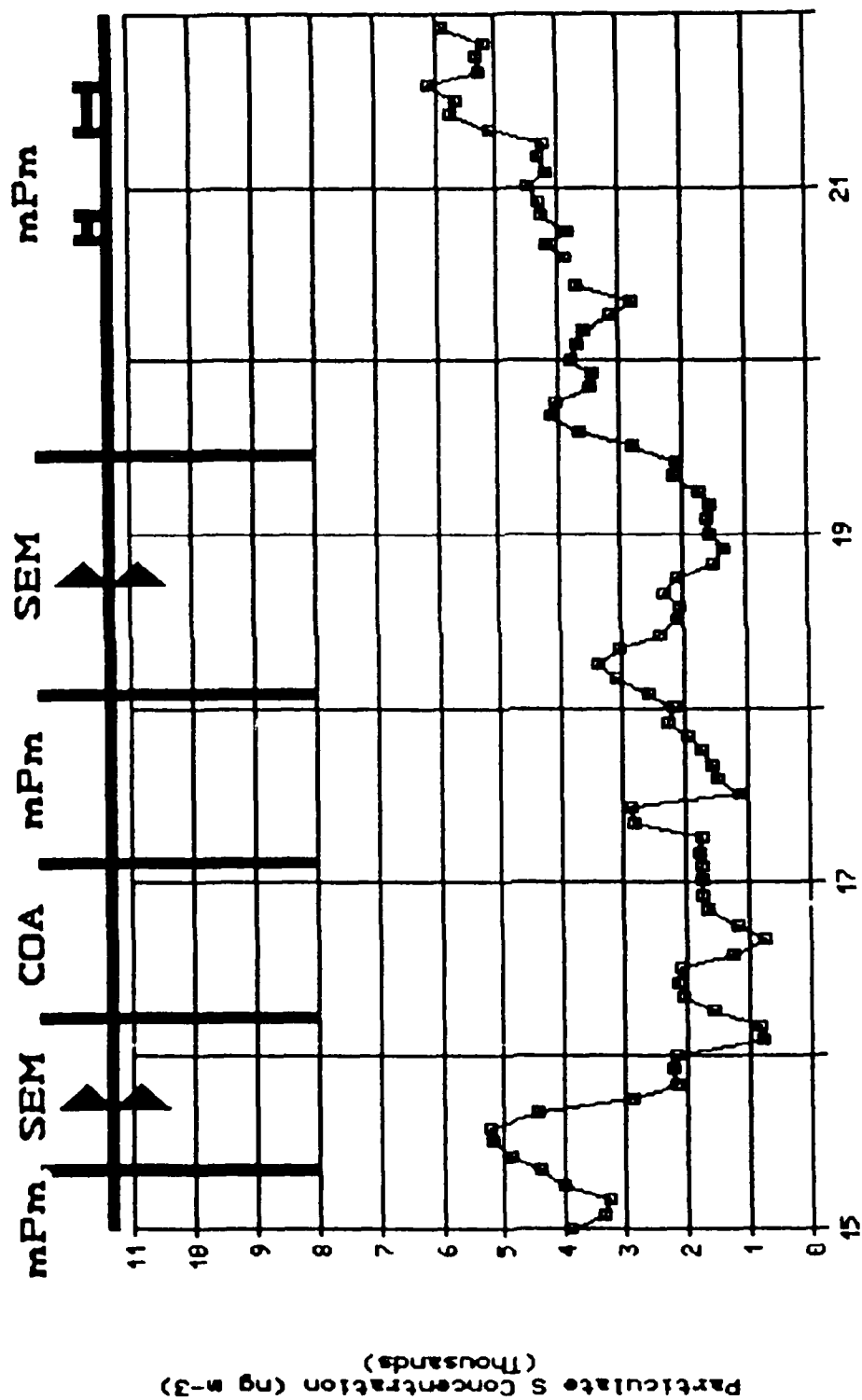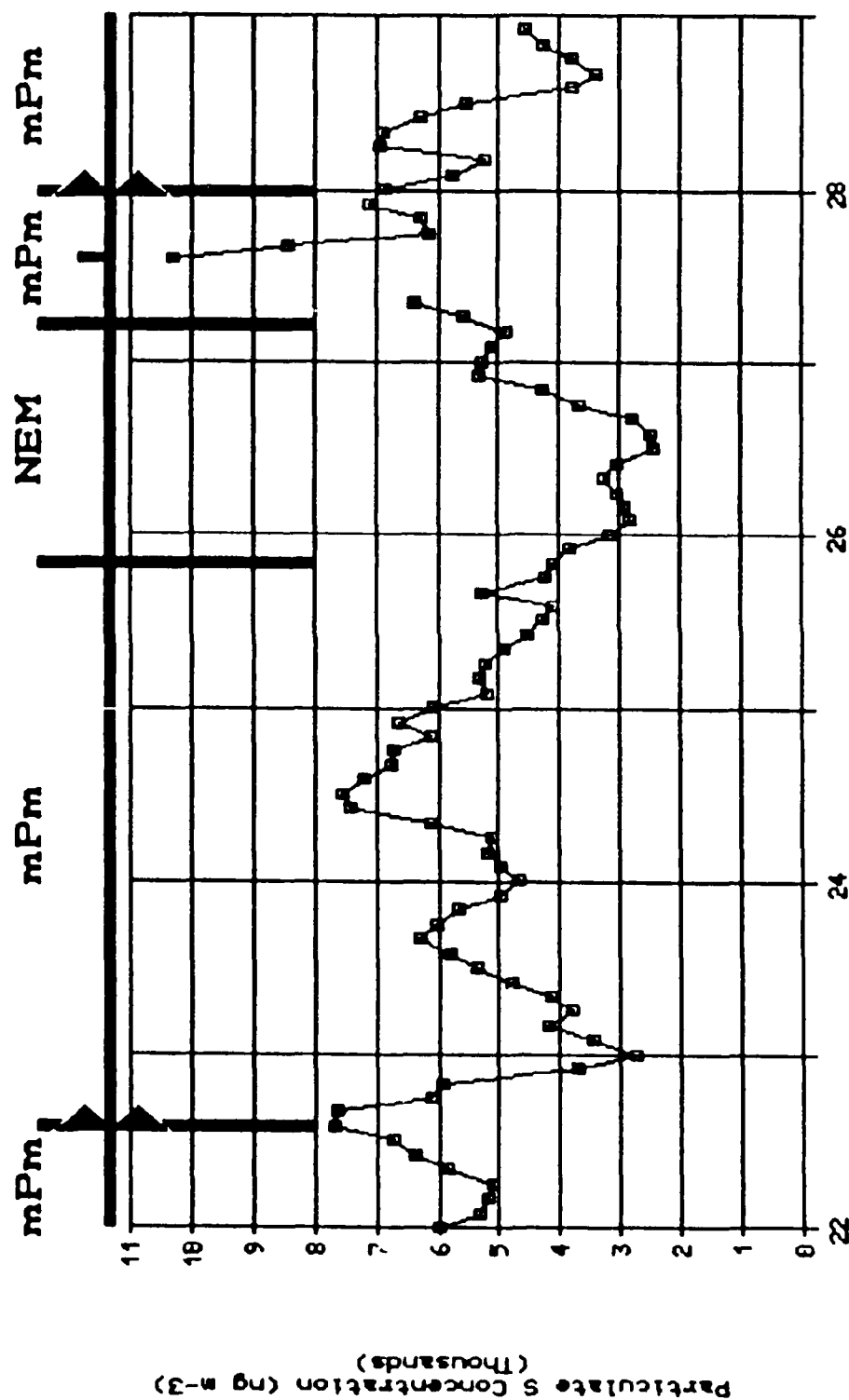Figure A.40 Atmospheric particulate sulfur concentration plotted every 2 hours (Eastern Daylight Time) at Ft. Wayne, IN (Site # 7) from October 15 through 21, 1977.
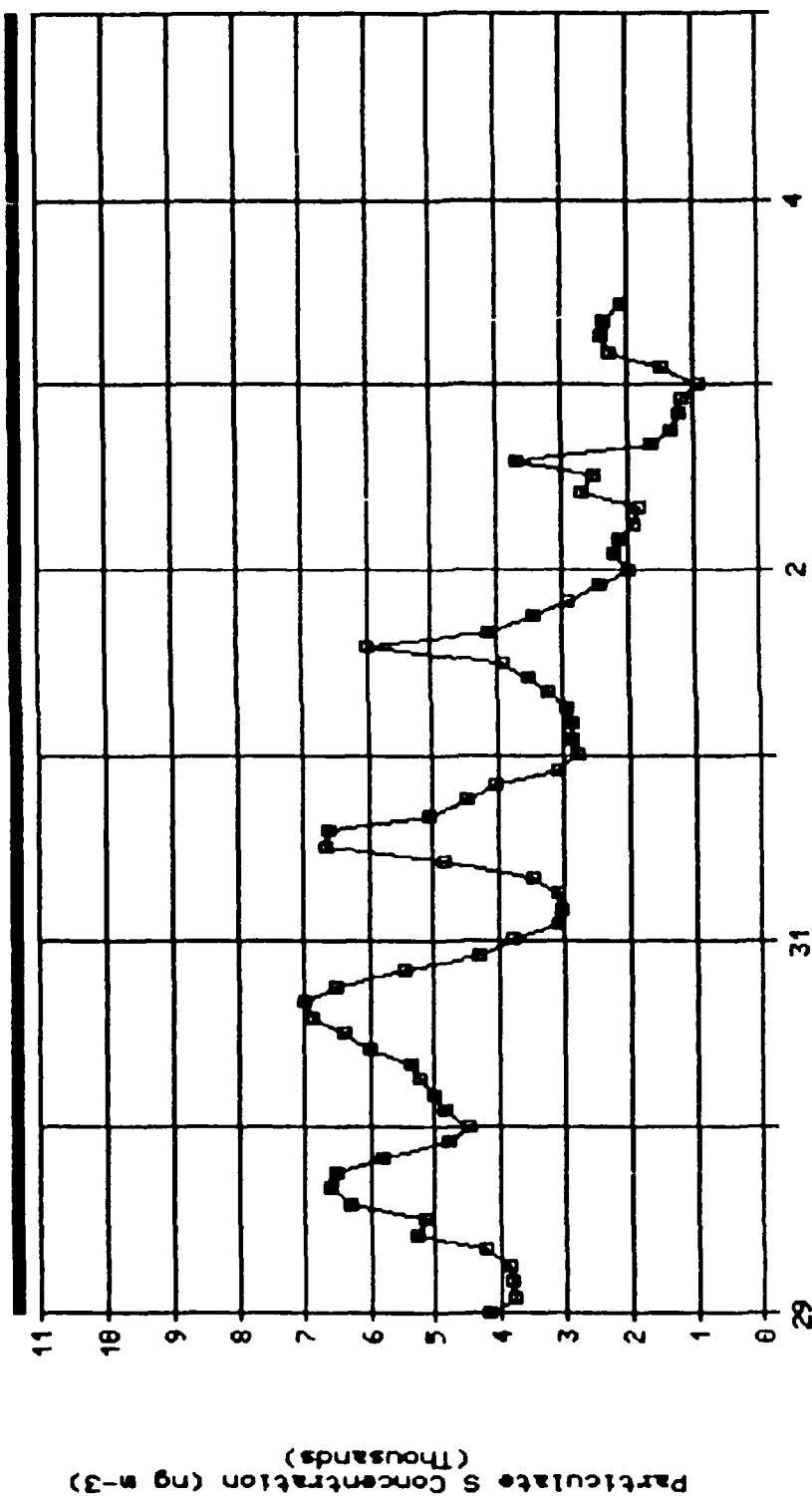
Figure A.41 Atmospheric particulate sulfur concentration plotted every 2 hours (Eastern Daylight Time) at Ft. Wayne, IN (Site # 7) from October 22 through 28, 1977.

mPm

Figure A.42 Atmospheric particulate sulfur concentration plotted every 2 hours (Eastern Daylight Time) at Ft. Wayne, IN (Site # 7) from October 29 through November 4, 1977.
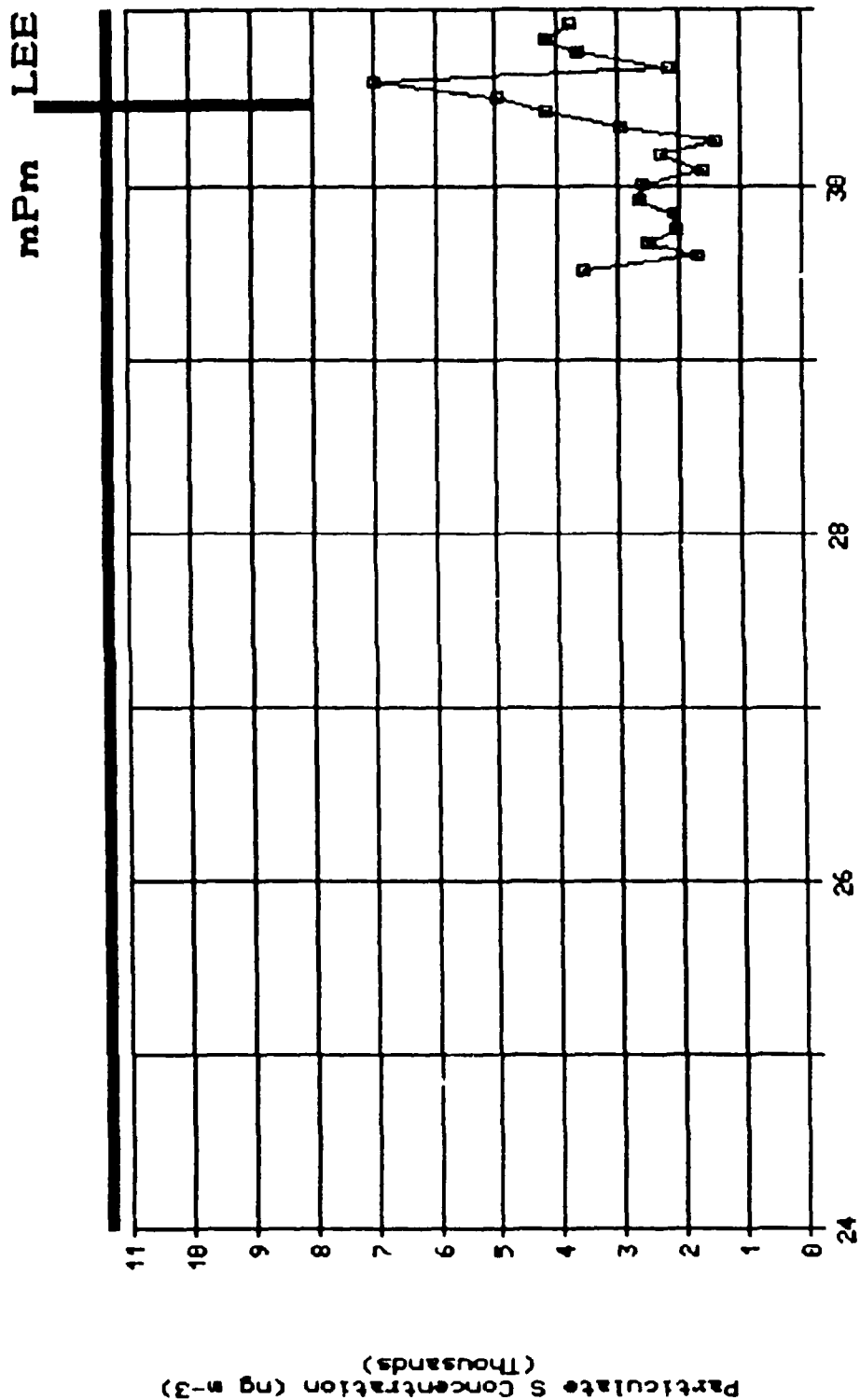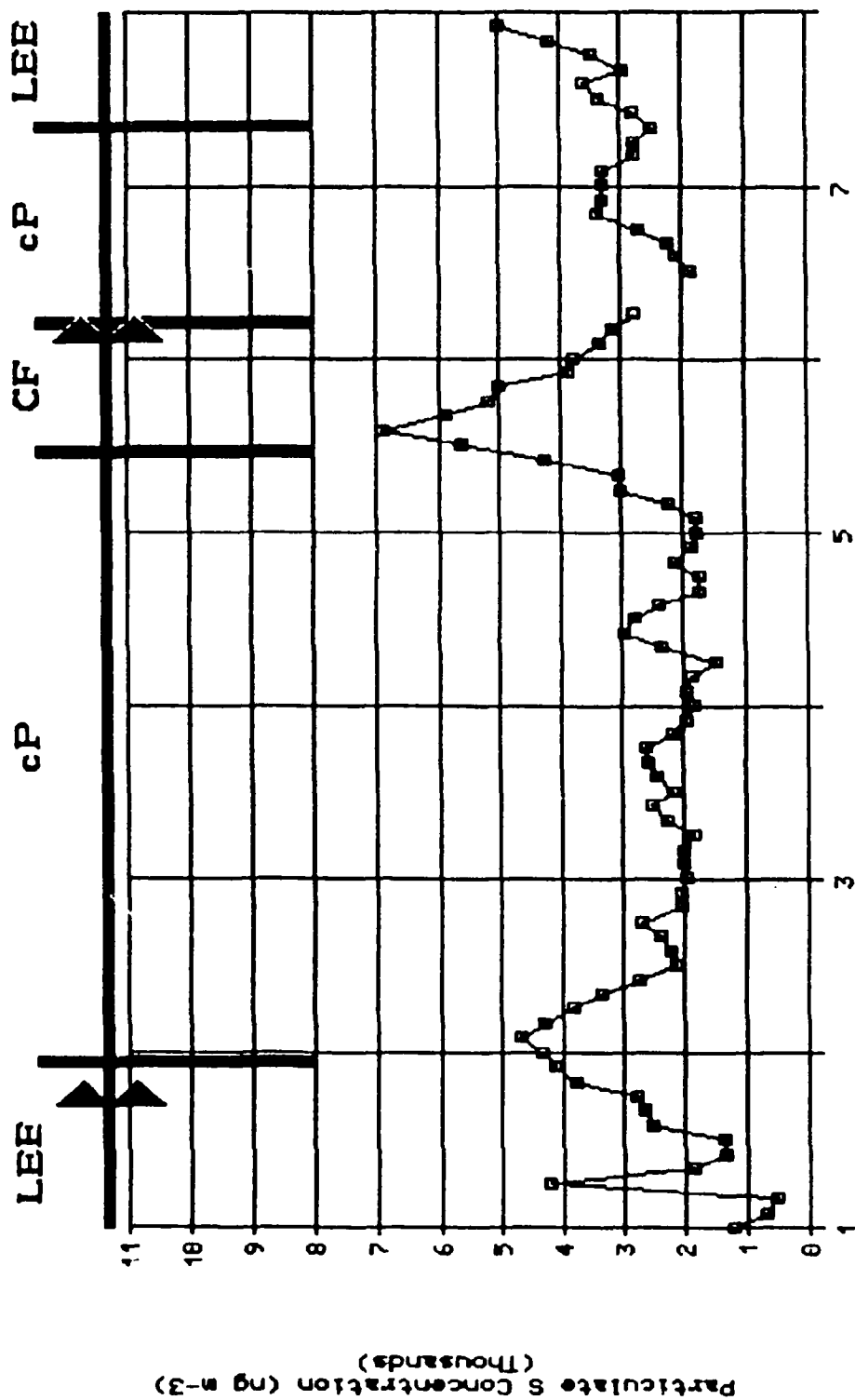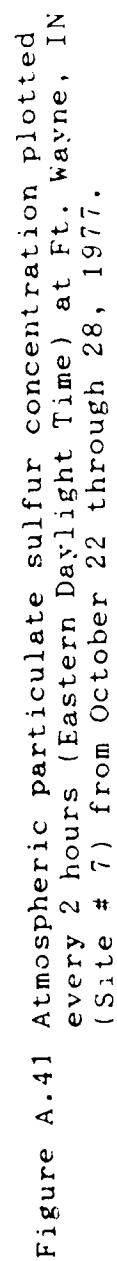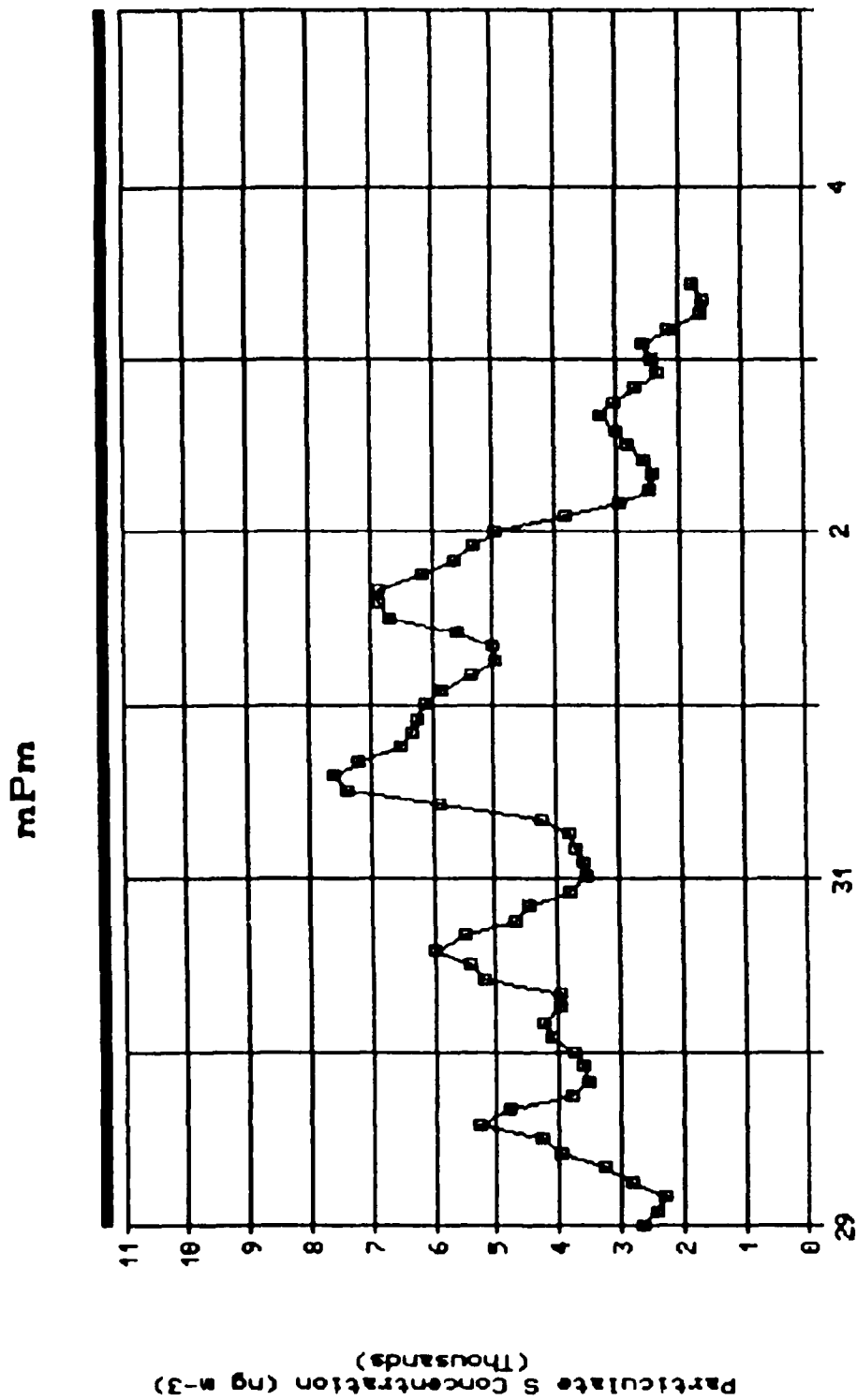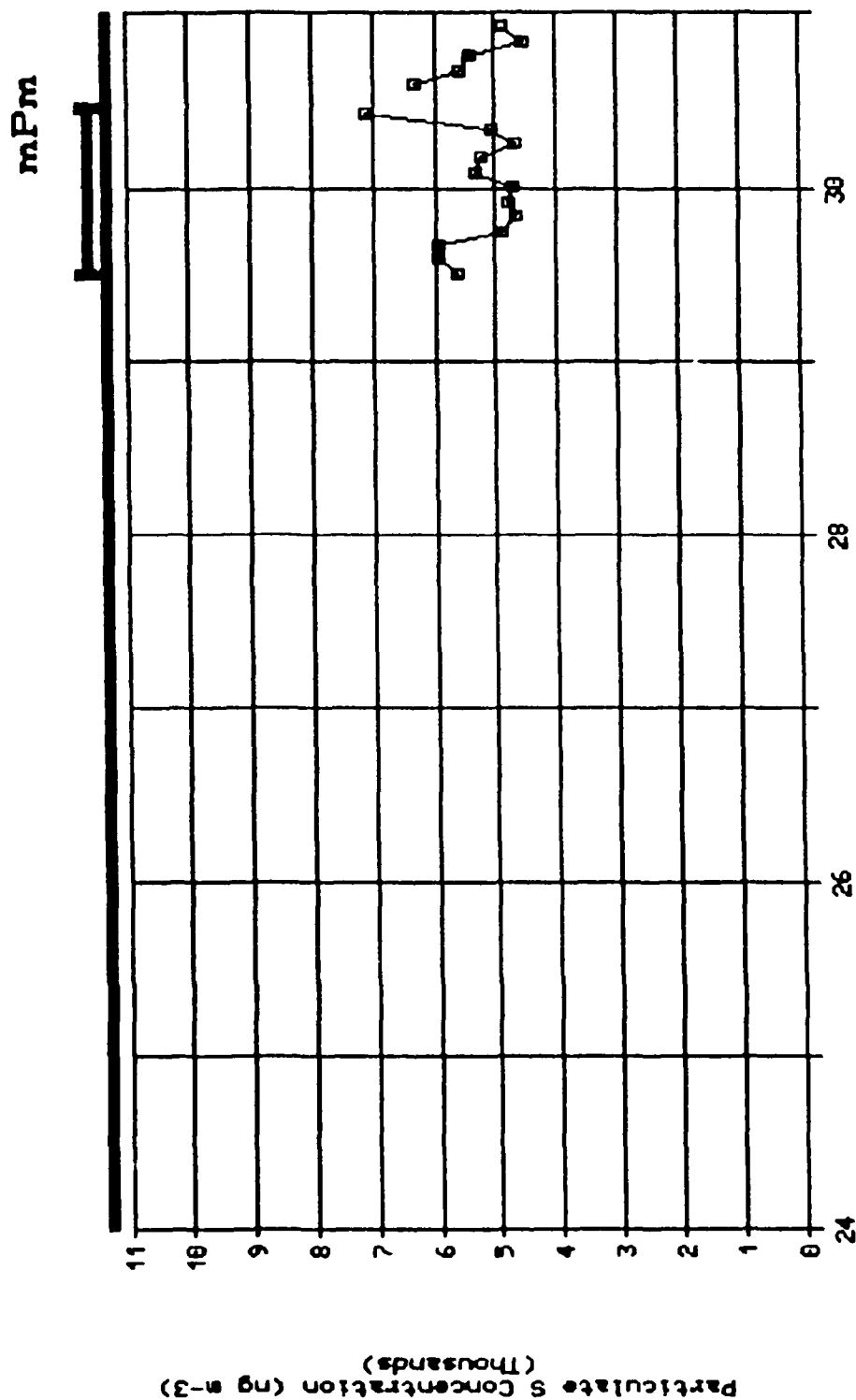
Figure A.43 Atmospheric particulate sulfur concentration plotted every 2 hours (Eastern Daylight Time) at Research Triangle Park, NC (Site # 8) from September 24 through 30, 1977.
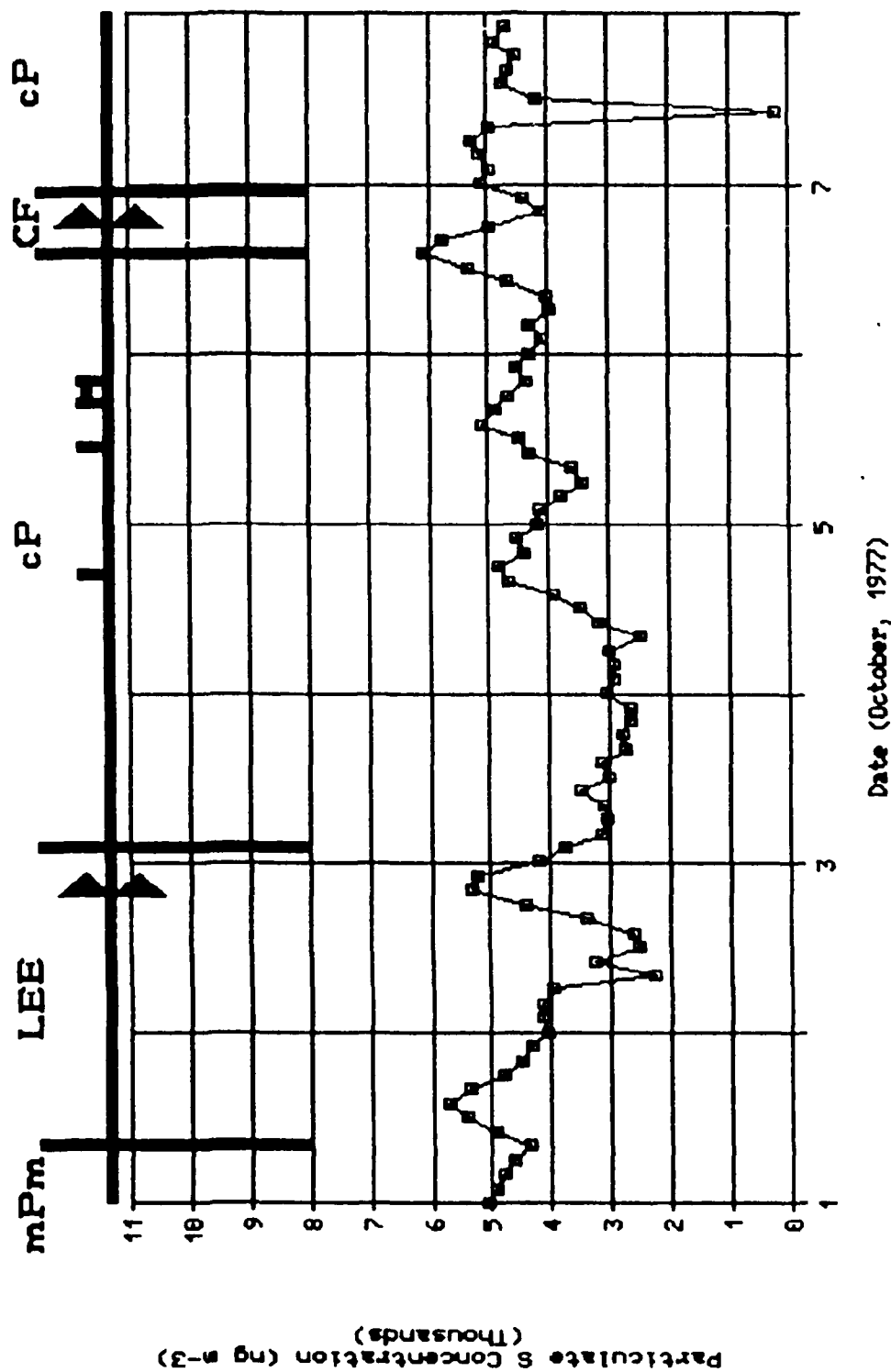
Figure A.44 Atmospheric particulate sulfur concentration plotted
every 2 hours (Eastern Daylight Time) at Research
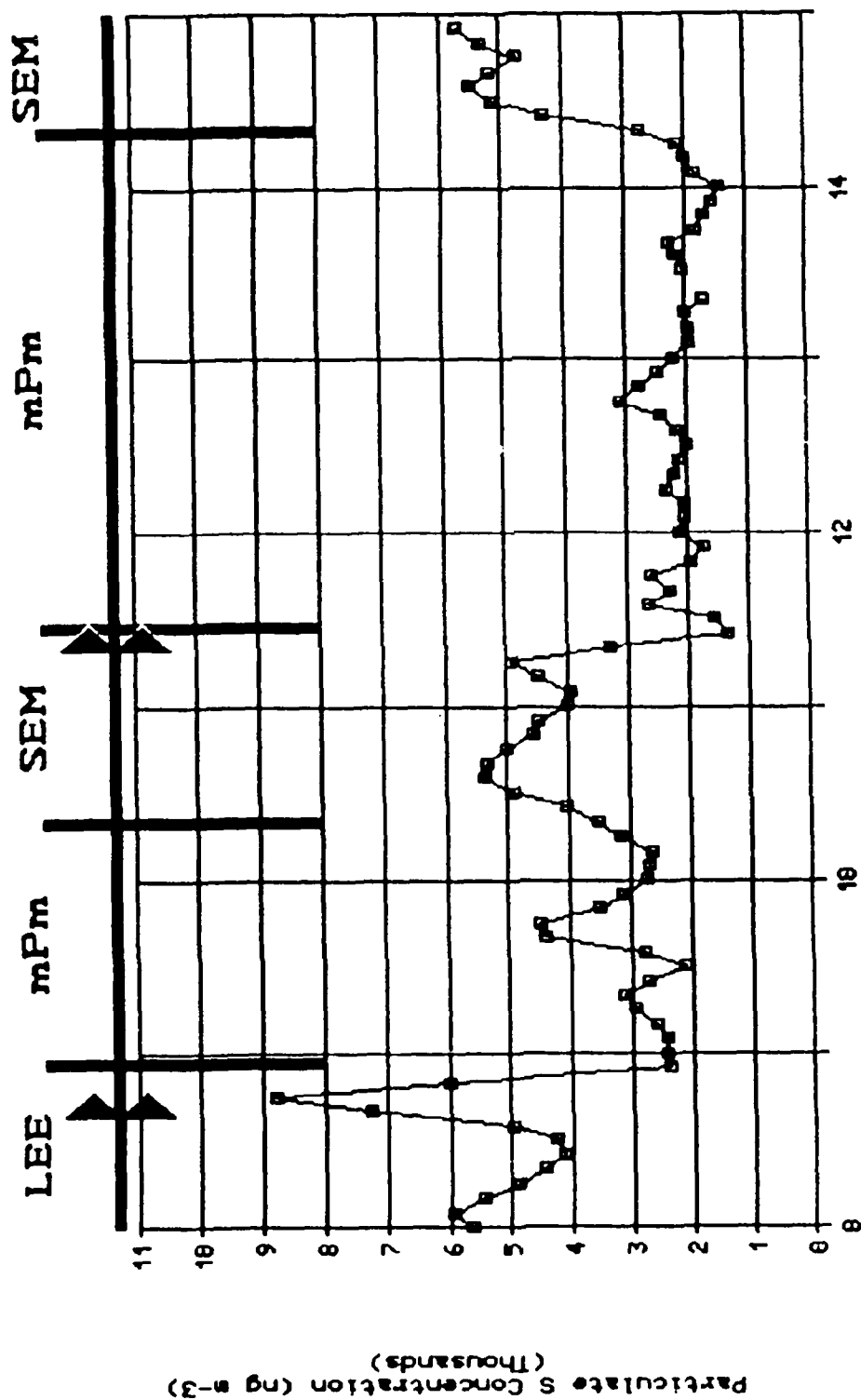Triangle Park, NC (Site # 8) from October 1 through 7,
1977.
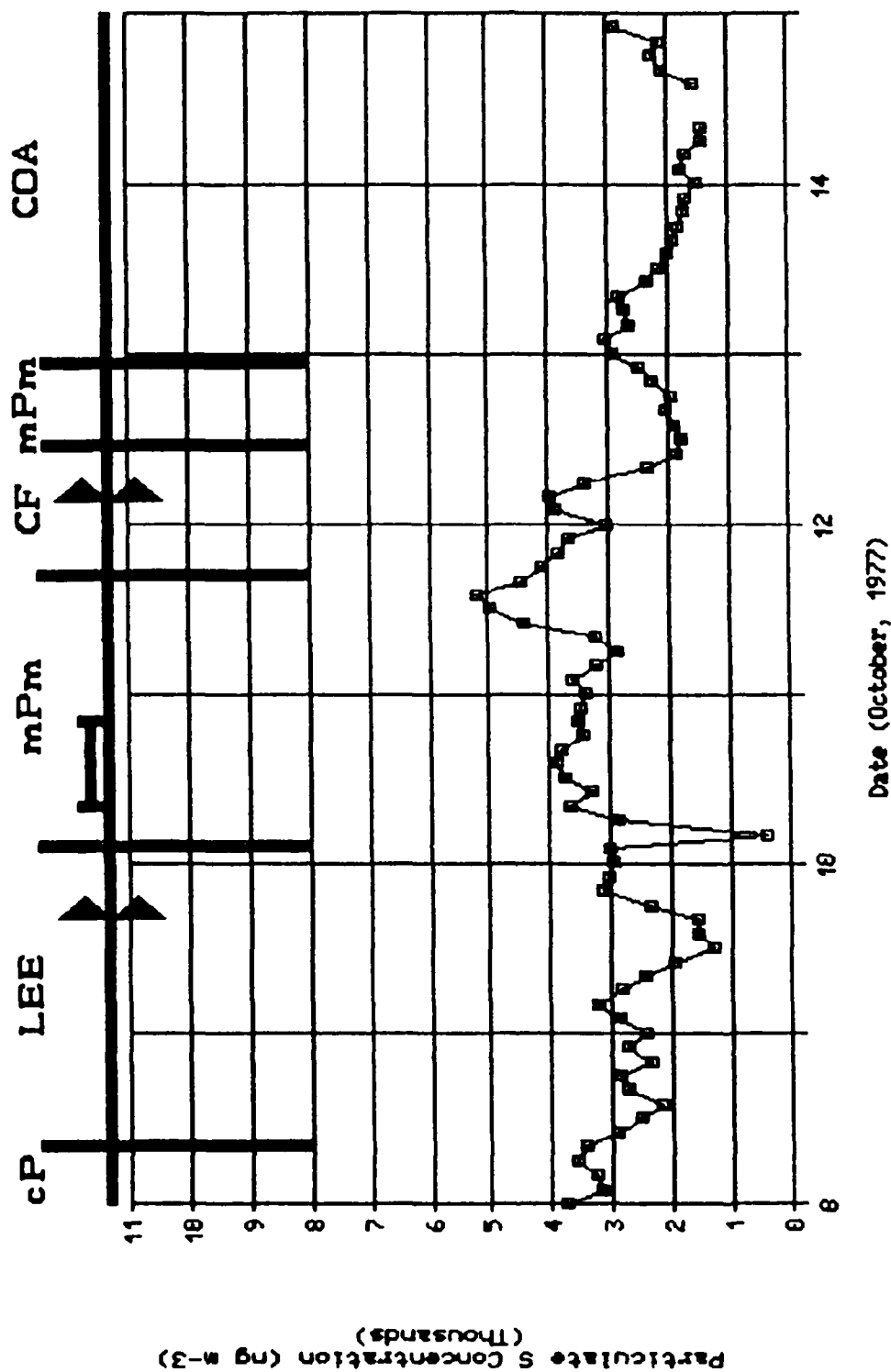
Figure A.45 Atmospheric particulate sulfur concentration plotted
every 2 hours (Eastern Daylight Time) at Research
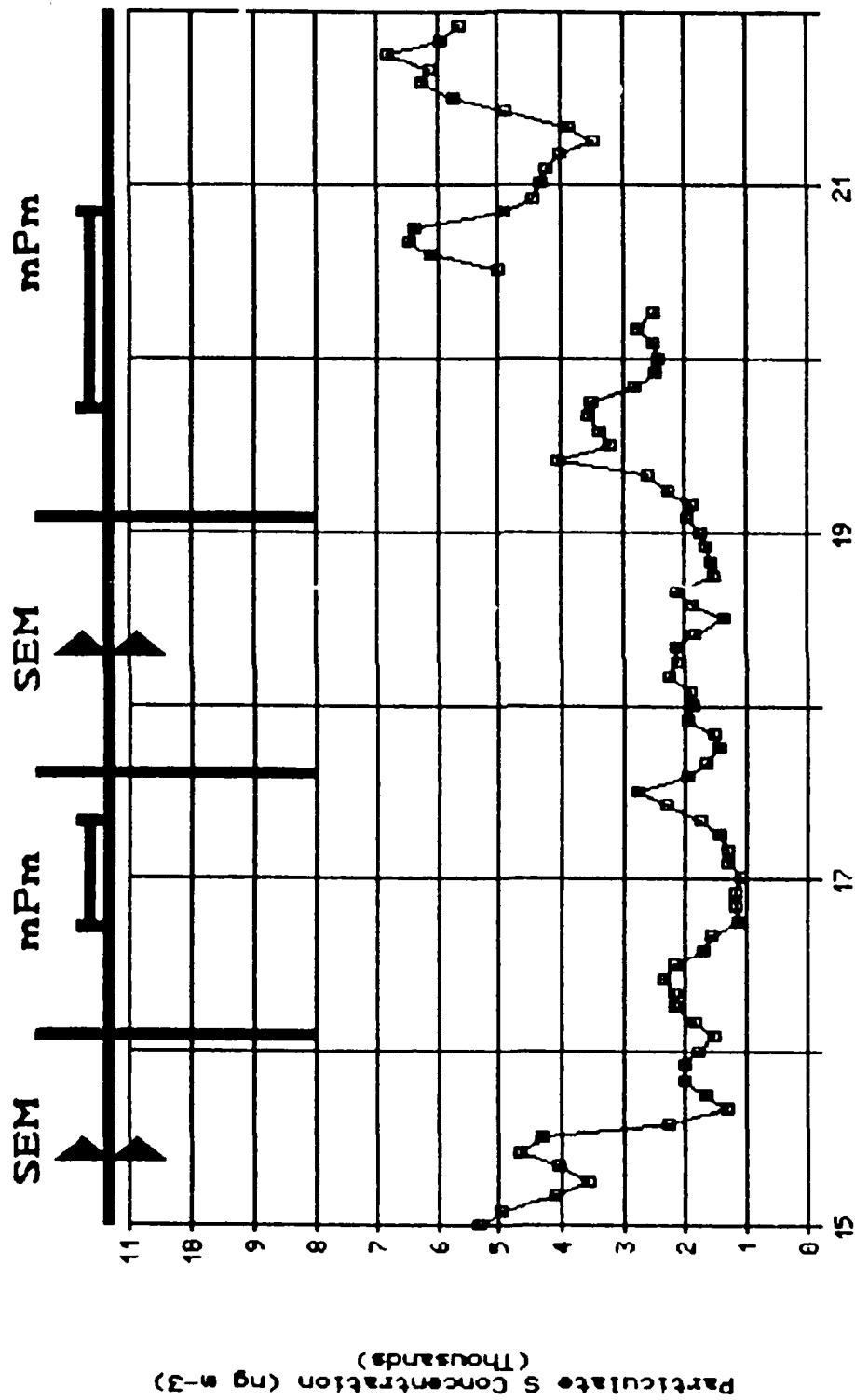Triangle Park, NC (Site # 8) from October 8 through 14,
1977.
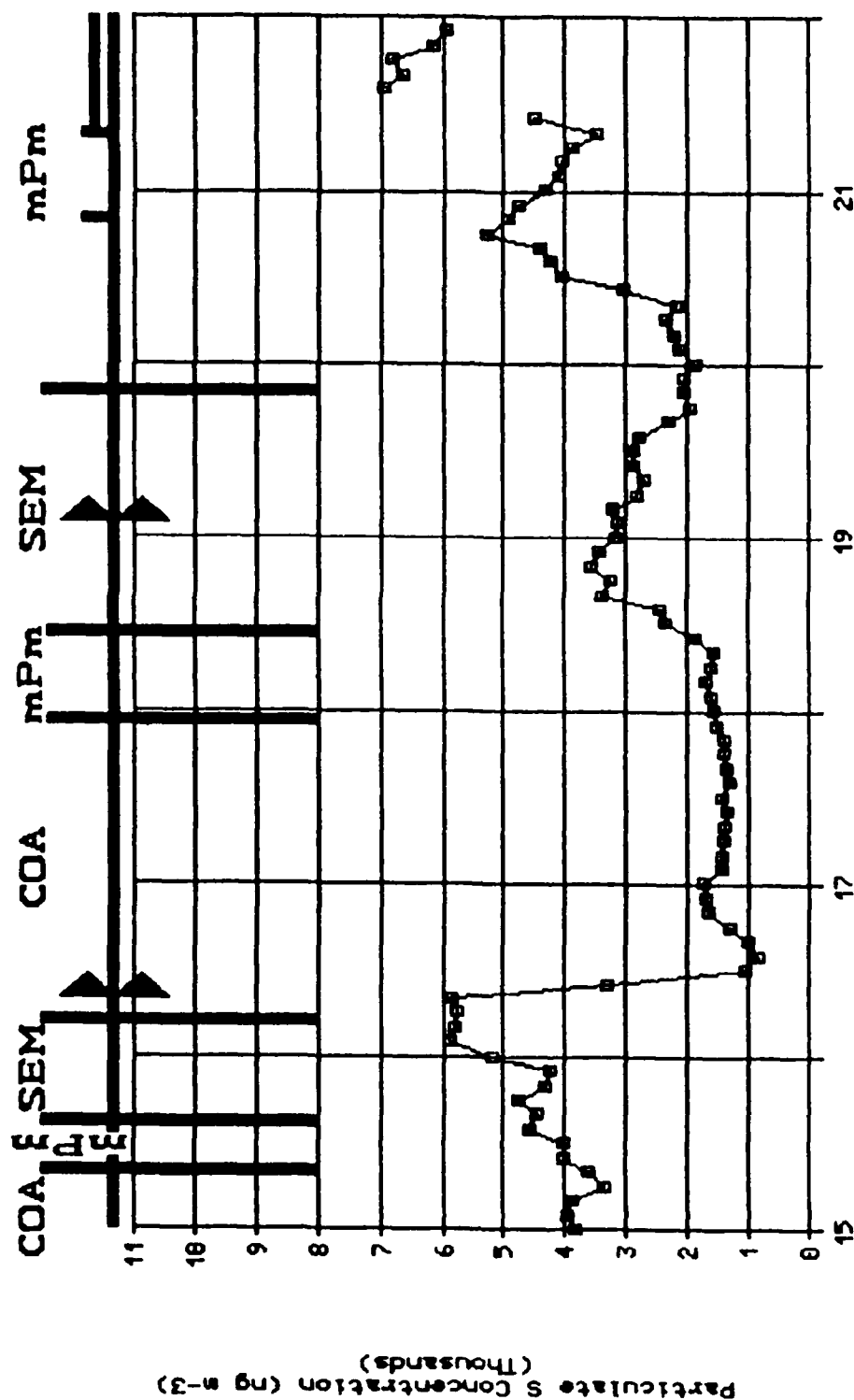
Figure A.46 Atmospheric particulate sulfur concentration plotted
every 2 hours (Eastern Daylight Time) at Research
Triangle Park, NC (Site # 8) from October 15 through
21, 1977.

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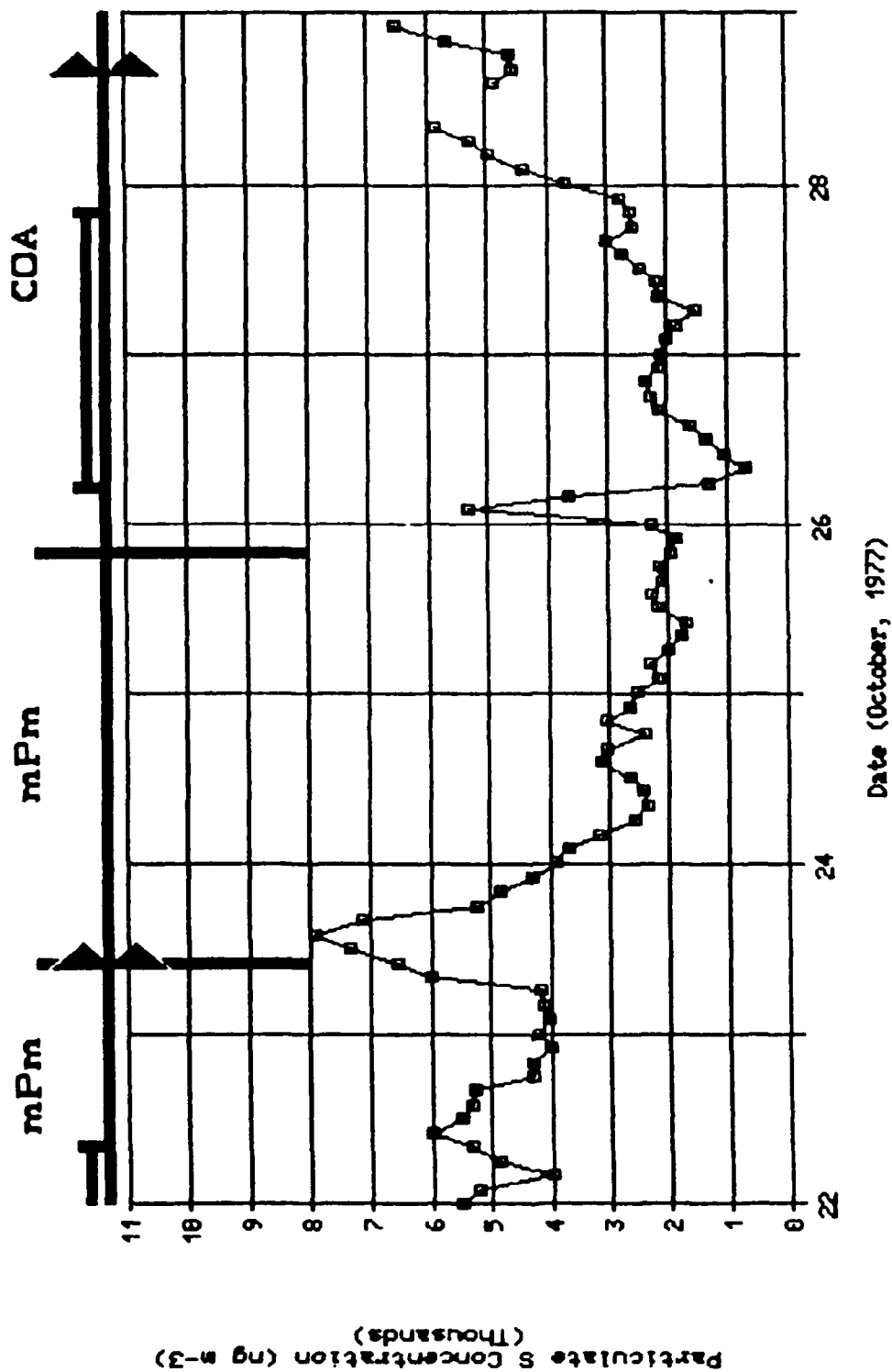
Figure A.47 Atmospheric particulate sulfur concentration plotted
every 2 hours (Eastern Daylight Time) at Research
Triangle Park, NC (Site # 8) from October 22 through
28, 1977.
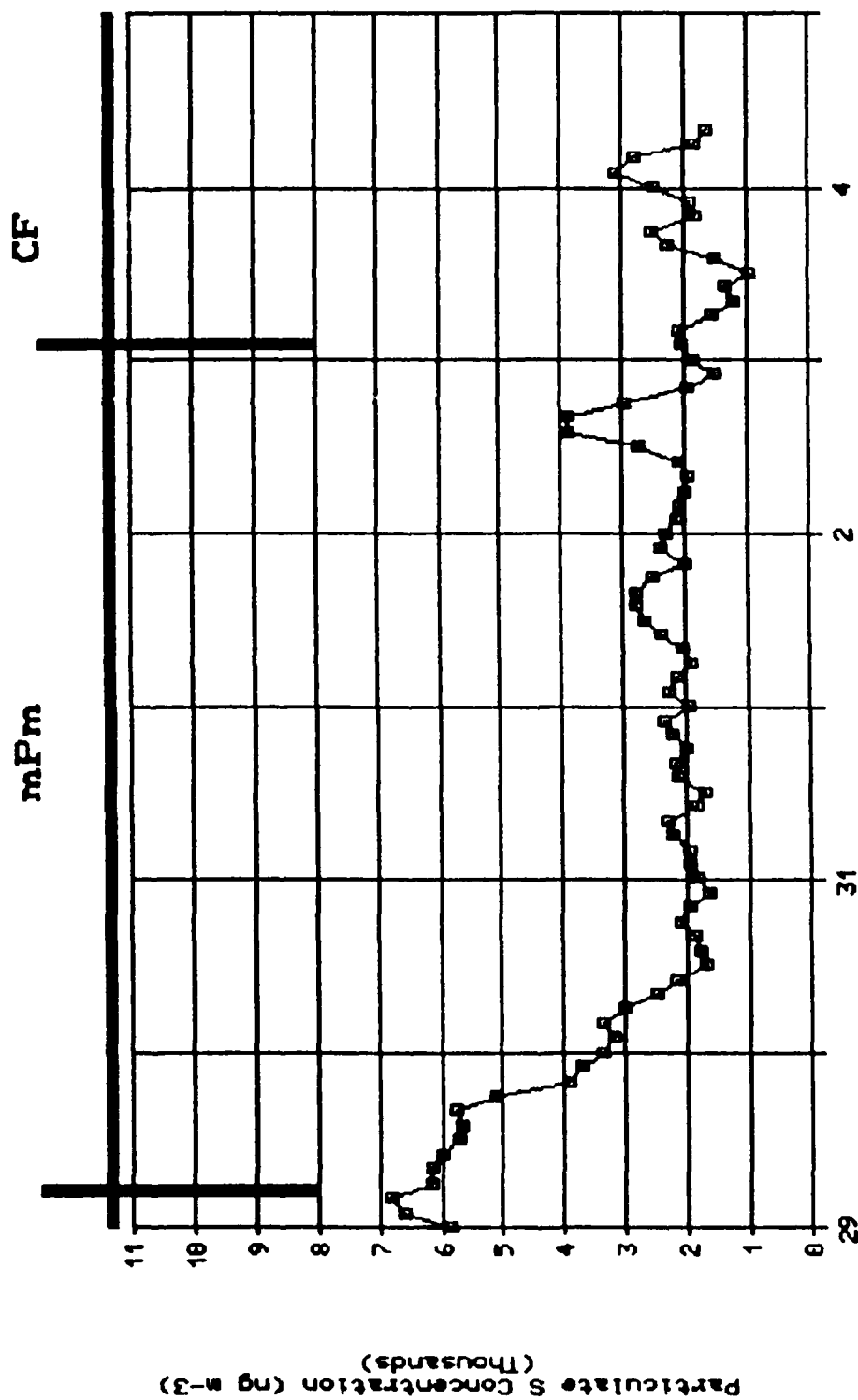
Figure A.48 Atmospheric particulate sulfur concentration plotted every 2 hours (Eastern Daylight Time) at Research Triangle Park, NC (Site #8) from October 29 through November 4, 1977.
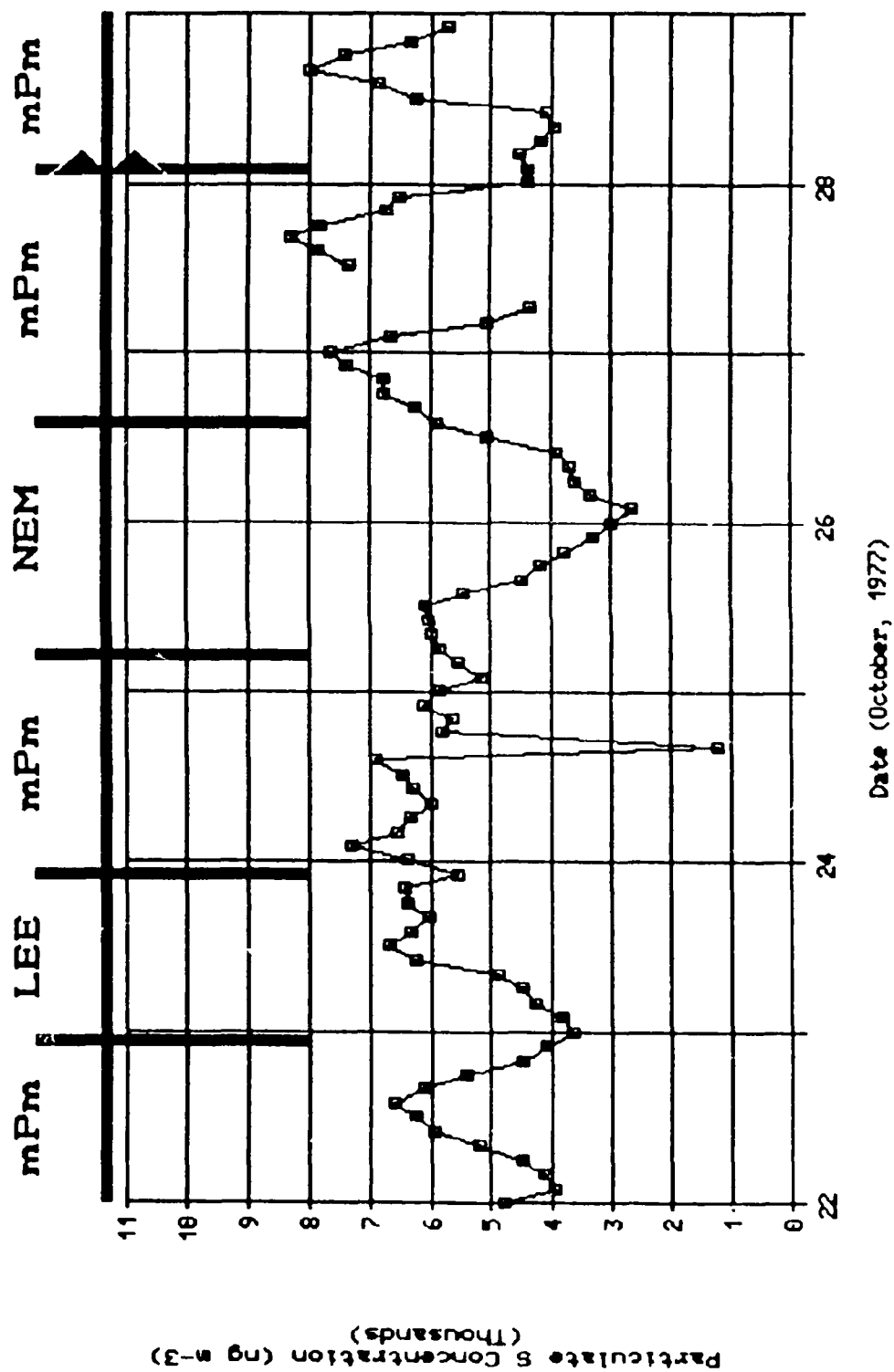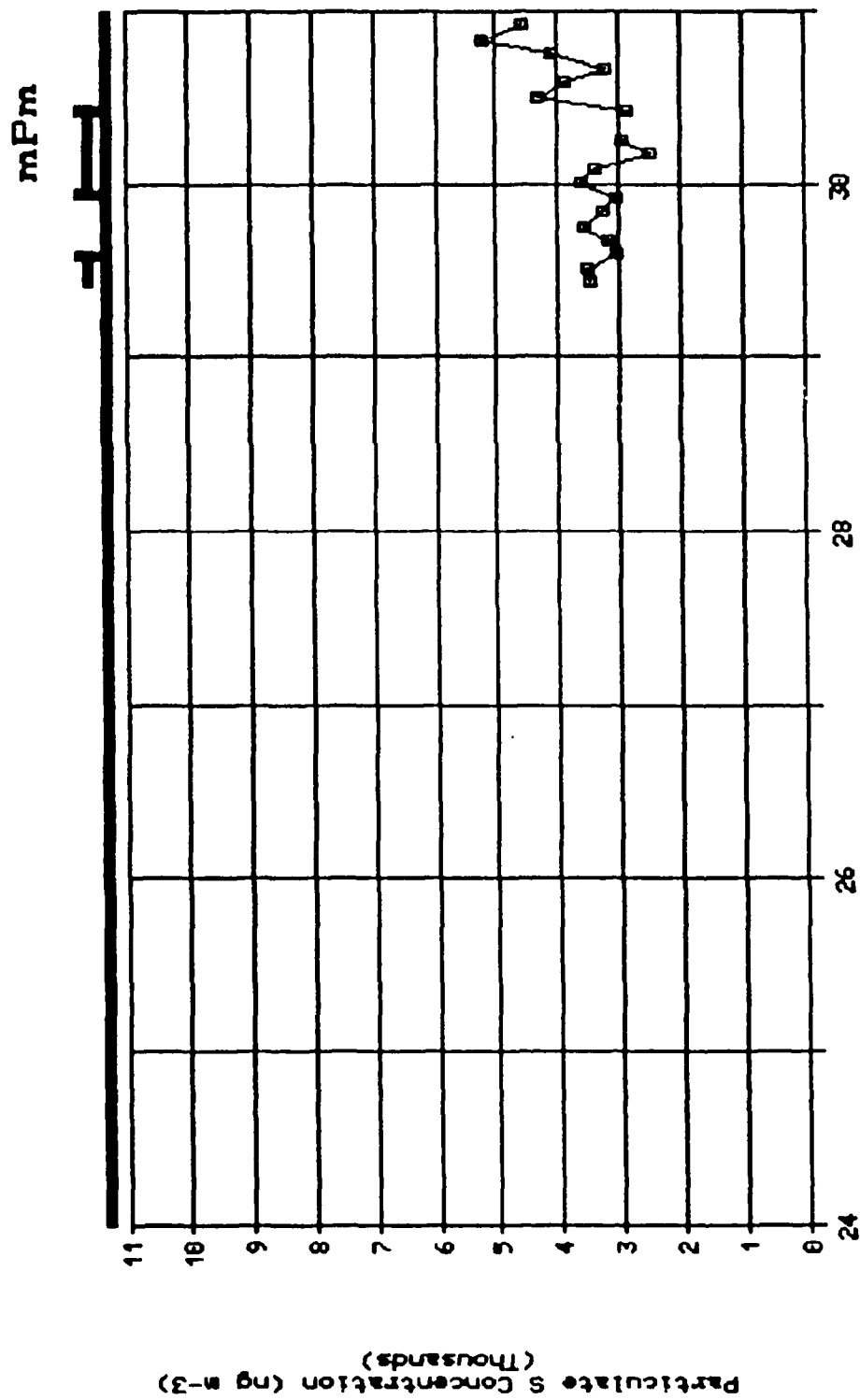
Figure A.49 Atmospheric particulate sulfur concentration plotted
every 2 hours (Eastern Daylight Time) at Ft. Wayne, IN
(Site # 7) from September 24 through 30, 1977.

Date (October, 1977)

Particulate S Concentration (ng m-3)
(Thousands)
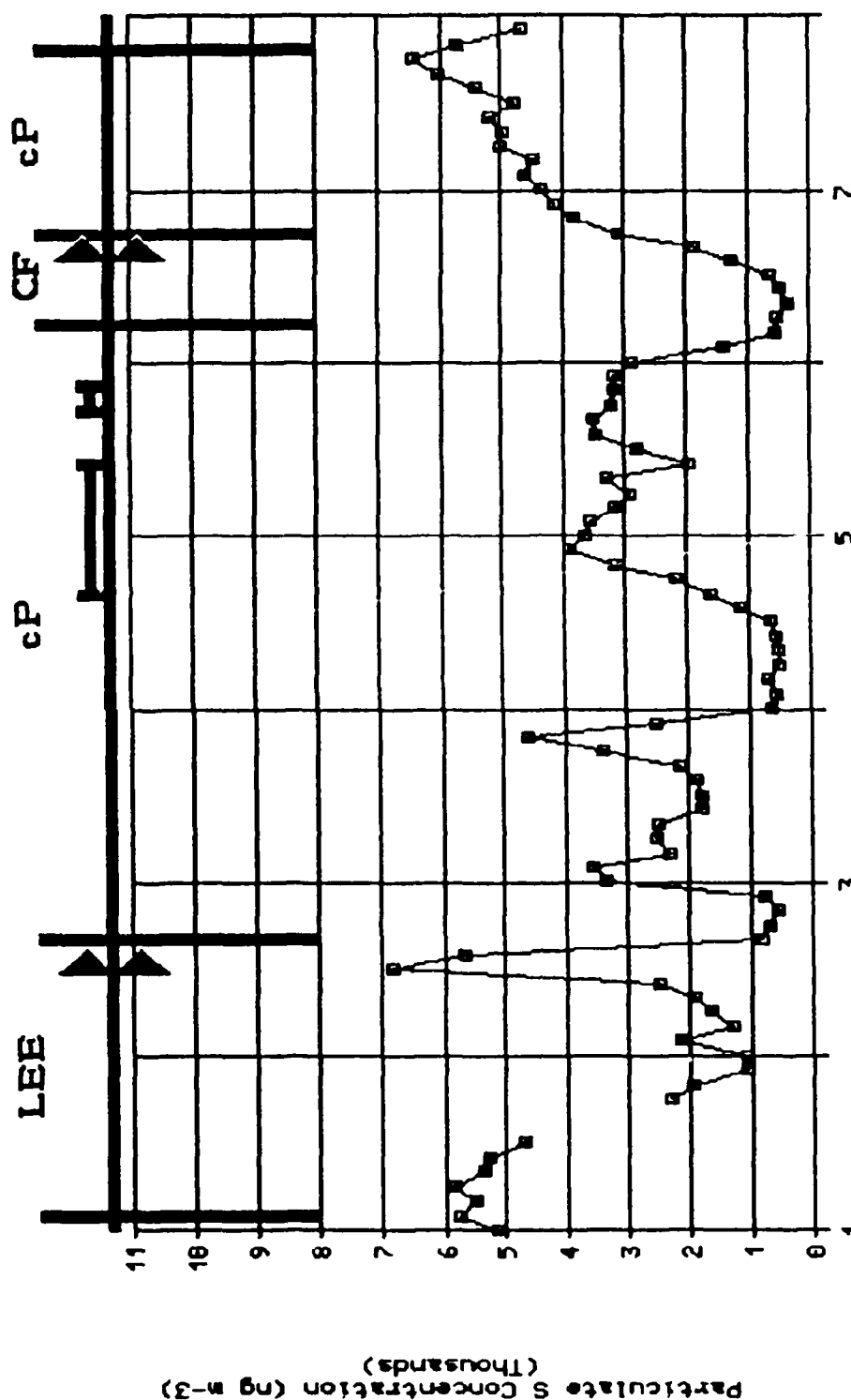
Figure A.50 Atmospheric particulate sulfur concentration plotted every 2 hours (Eastern Daylight Time) at Ft. Wayne, IN (Site # 7) from October 1 through 7, 1977.
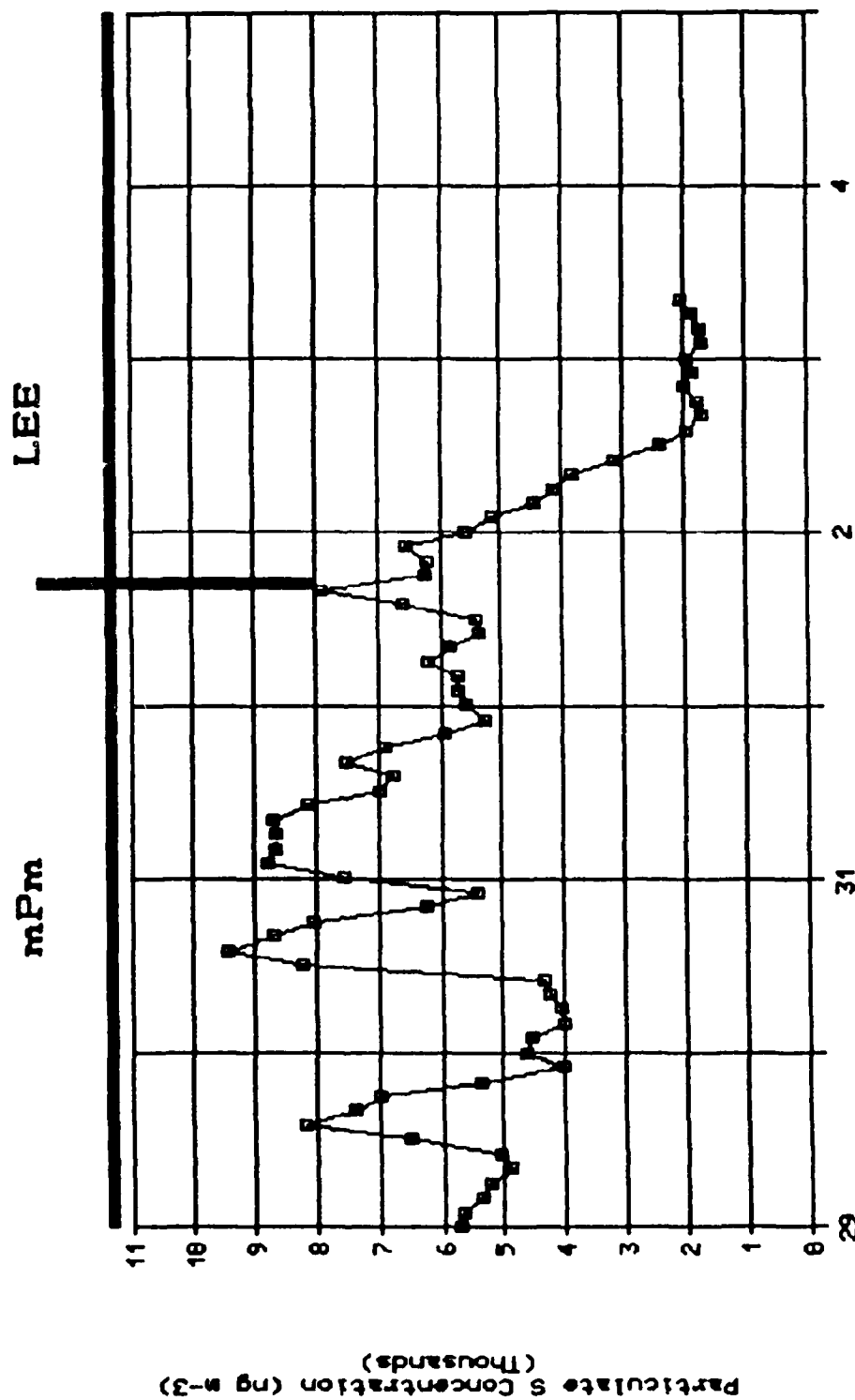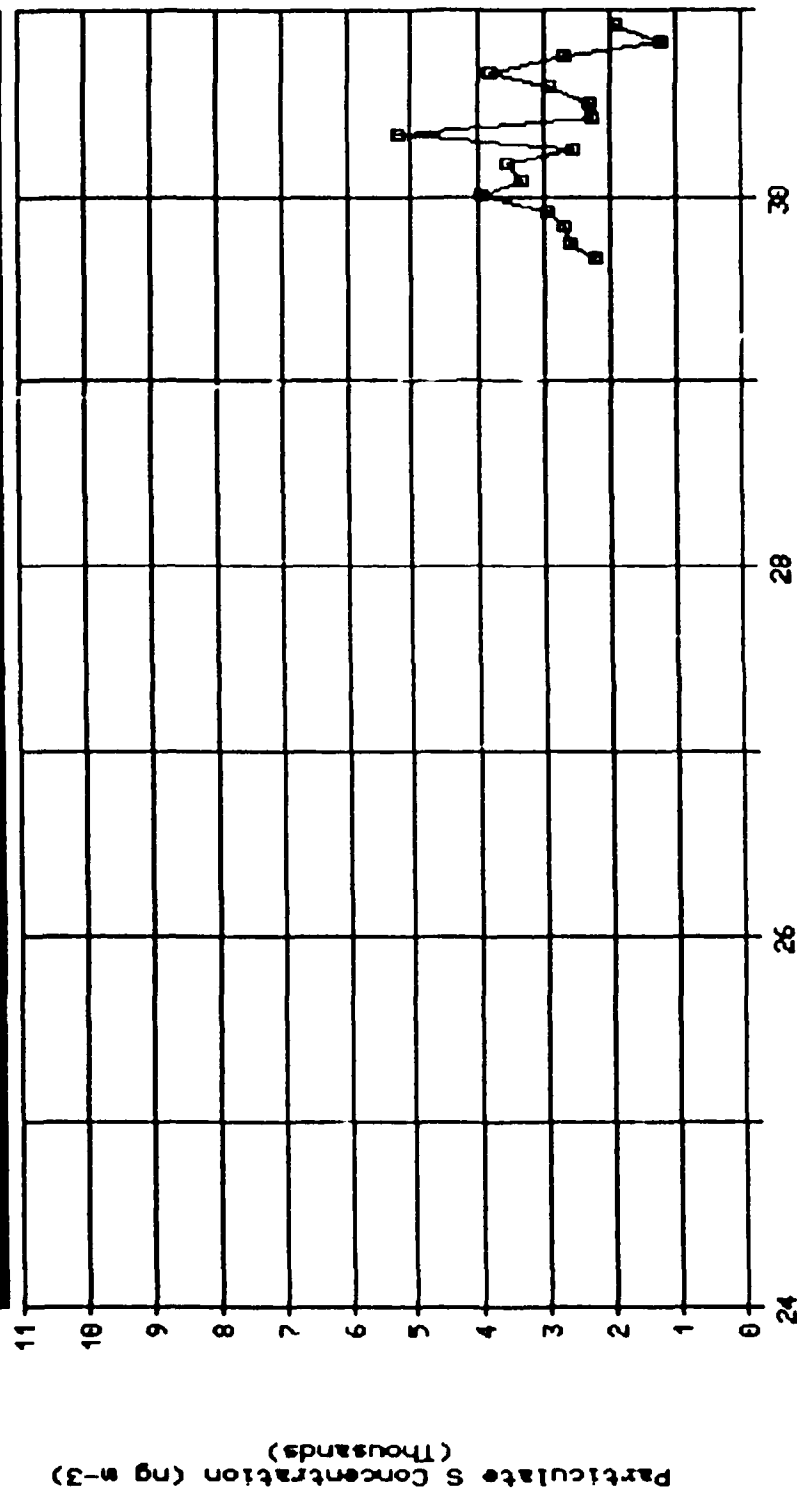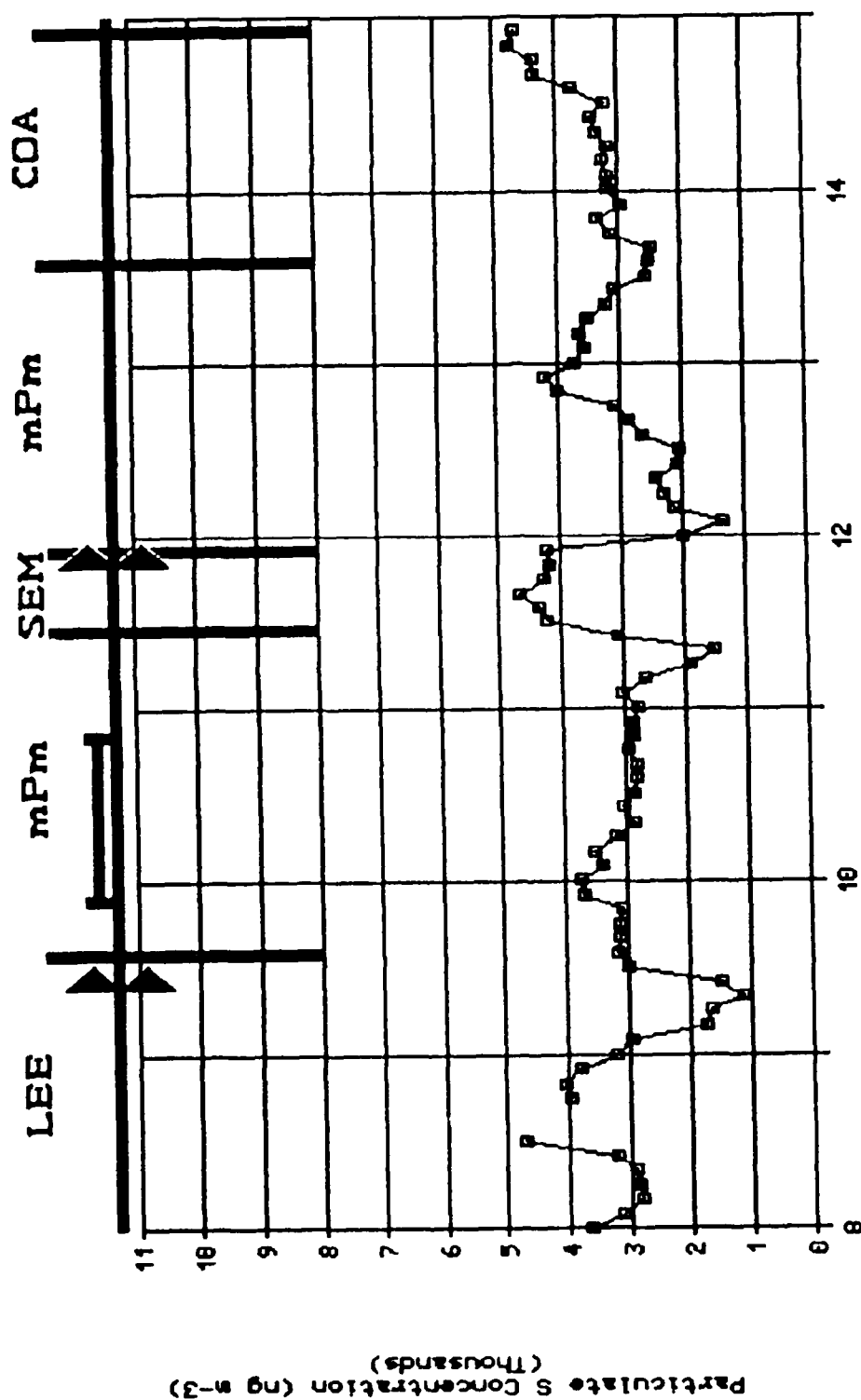
Figure A.51 Atmospheric particulate sulfur concentration plotted every 2 hours (Eastern Daylight Time) at FT. Wayne, IN (Site # 7) from October 8 through 14, 1977.
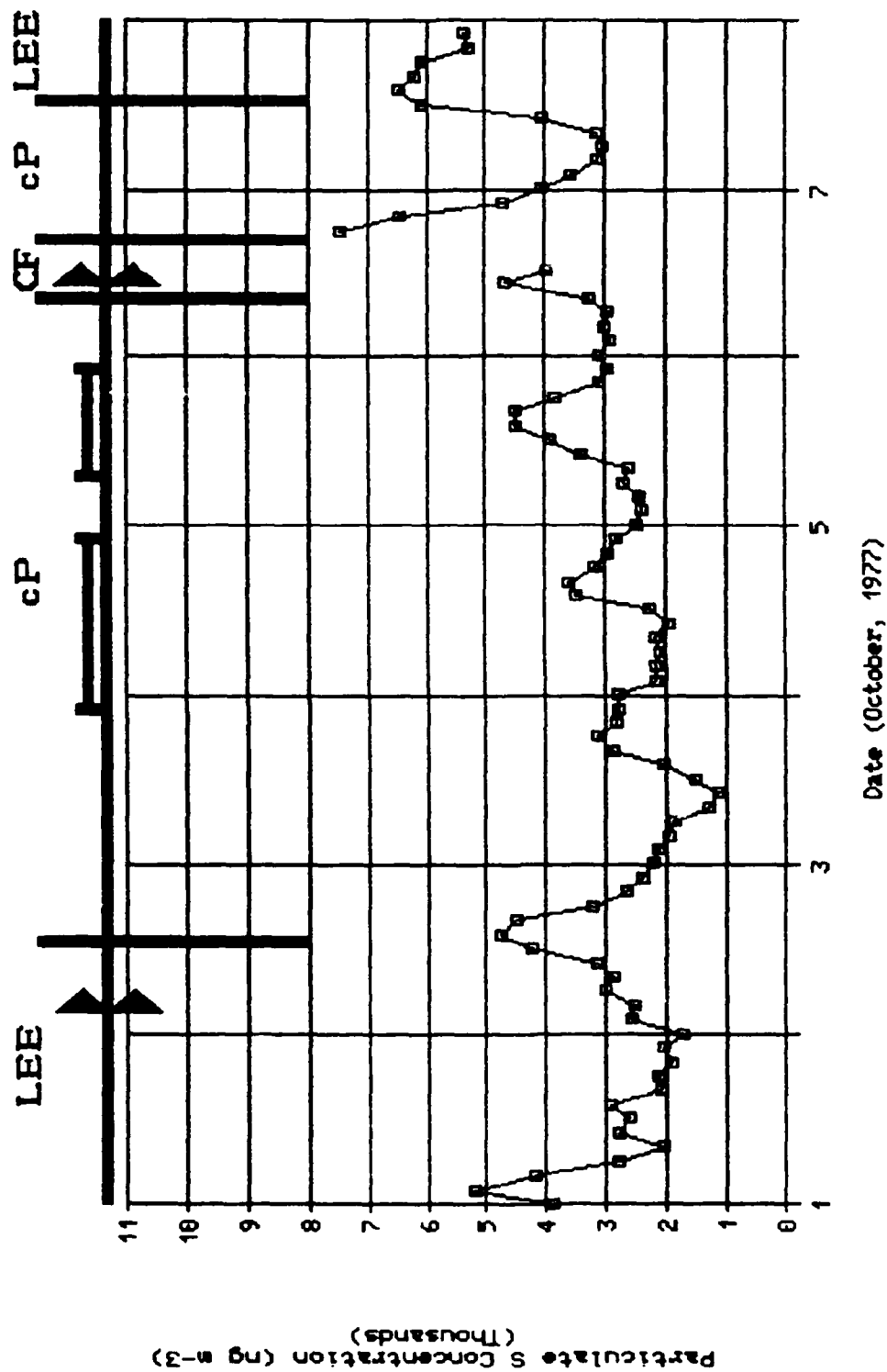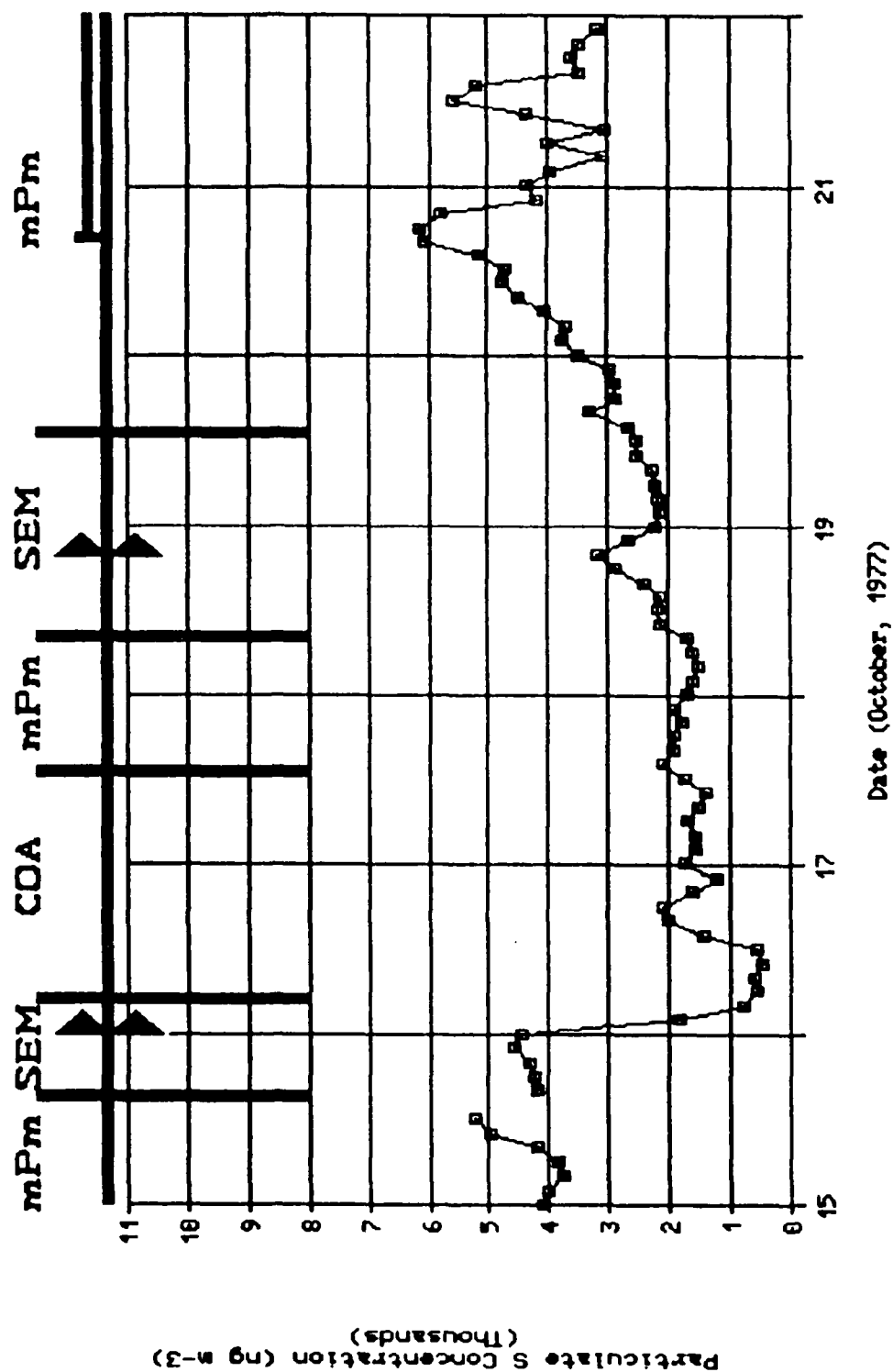
Figure A.52 Atmospheric particulate sulfur concentration plotted
every 2 hours (Eastern Daylight Time) at Ft. Wayne, IN
(Site # 7) from October 15 through 21, 1977.
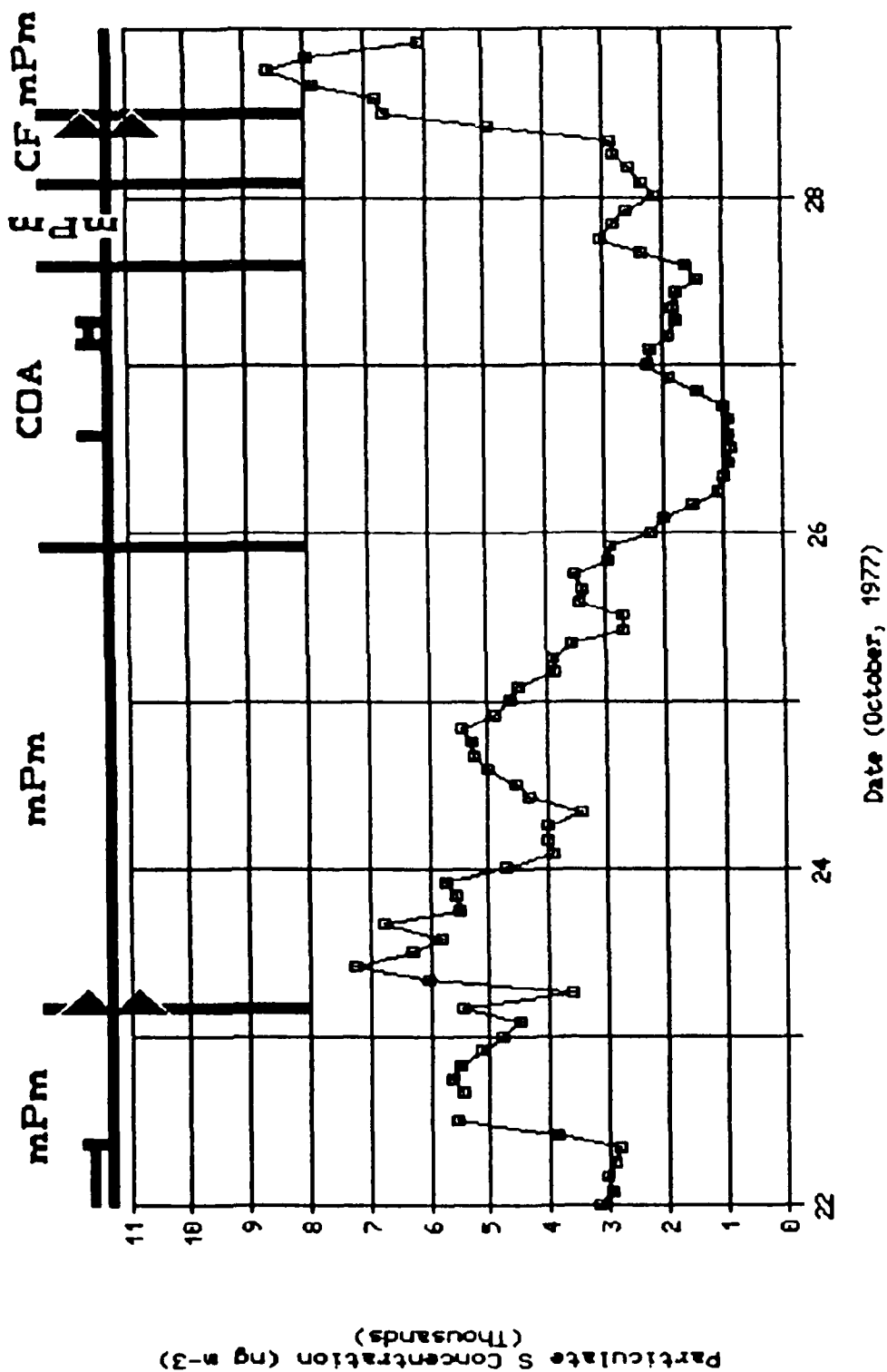
Figure A.53 Atmospheric particulate sulfur concentration plotted every 2 hours (Eastern Daylight Time) at Ft. Wayne, IN (Site # 7) from October 22 through 28, 1977.

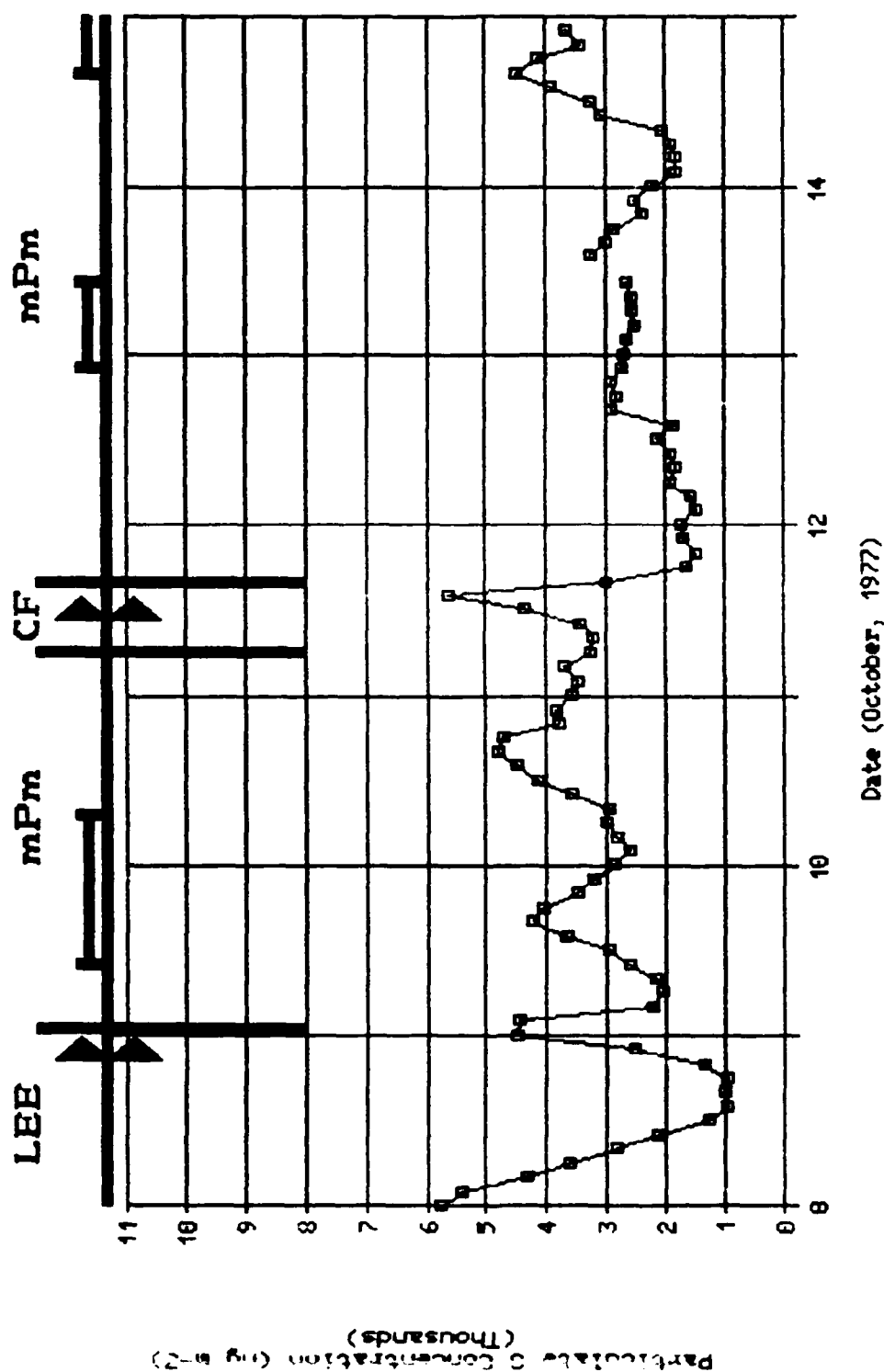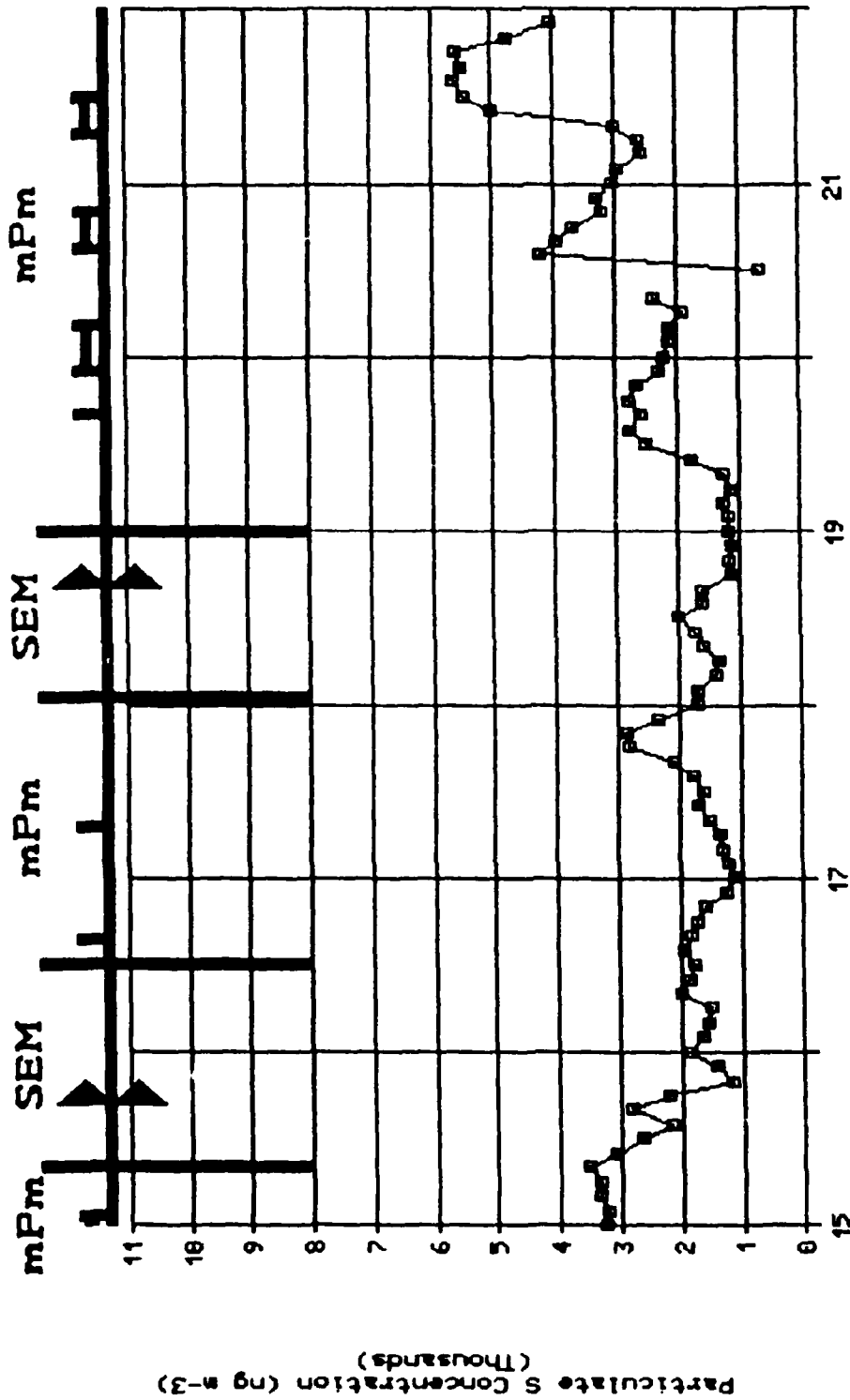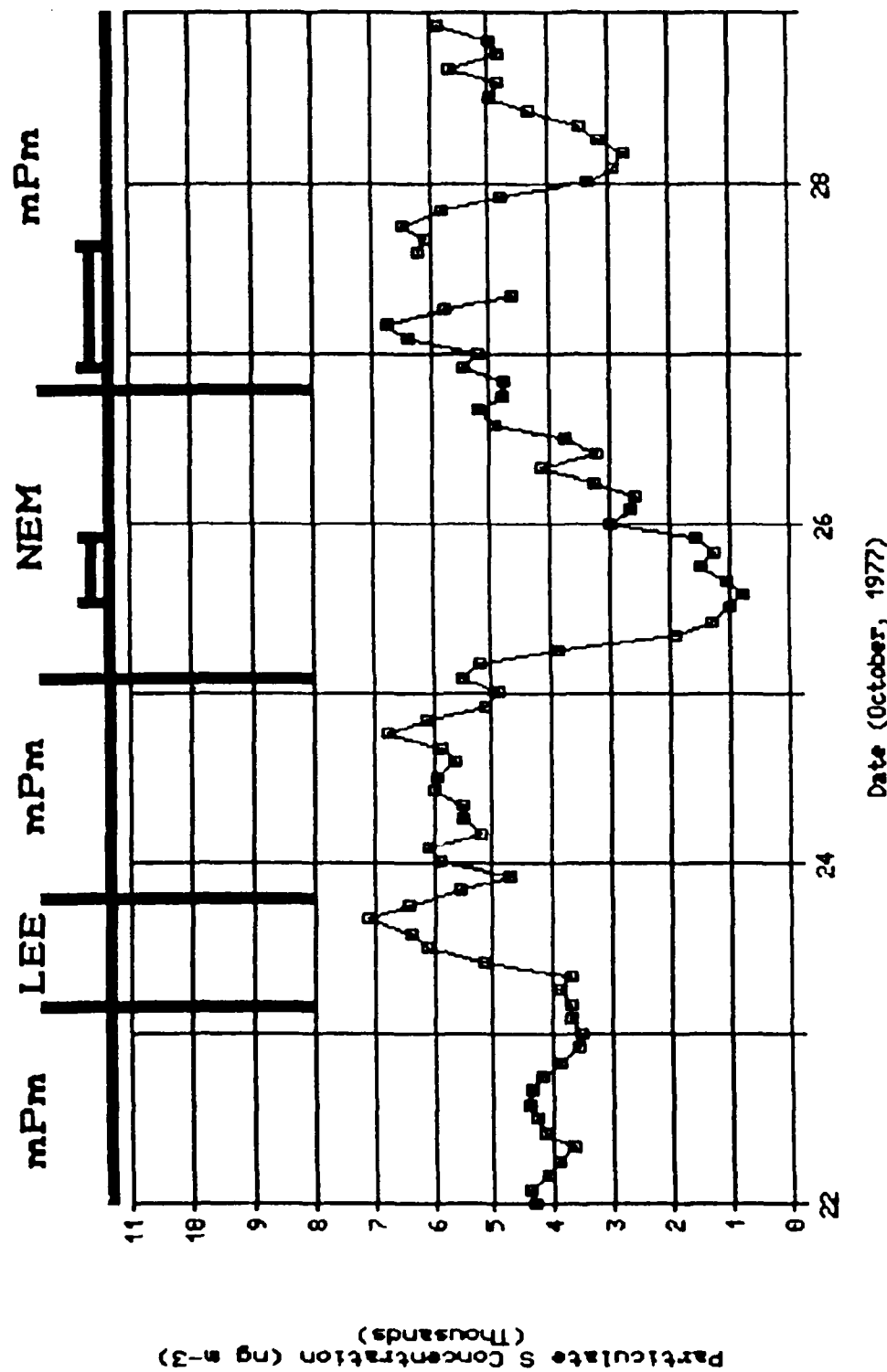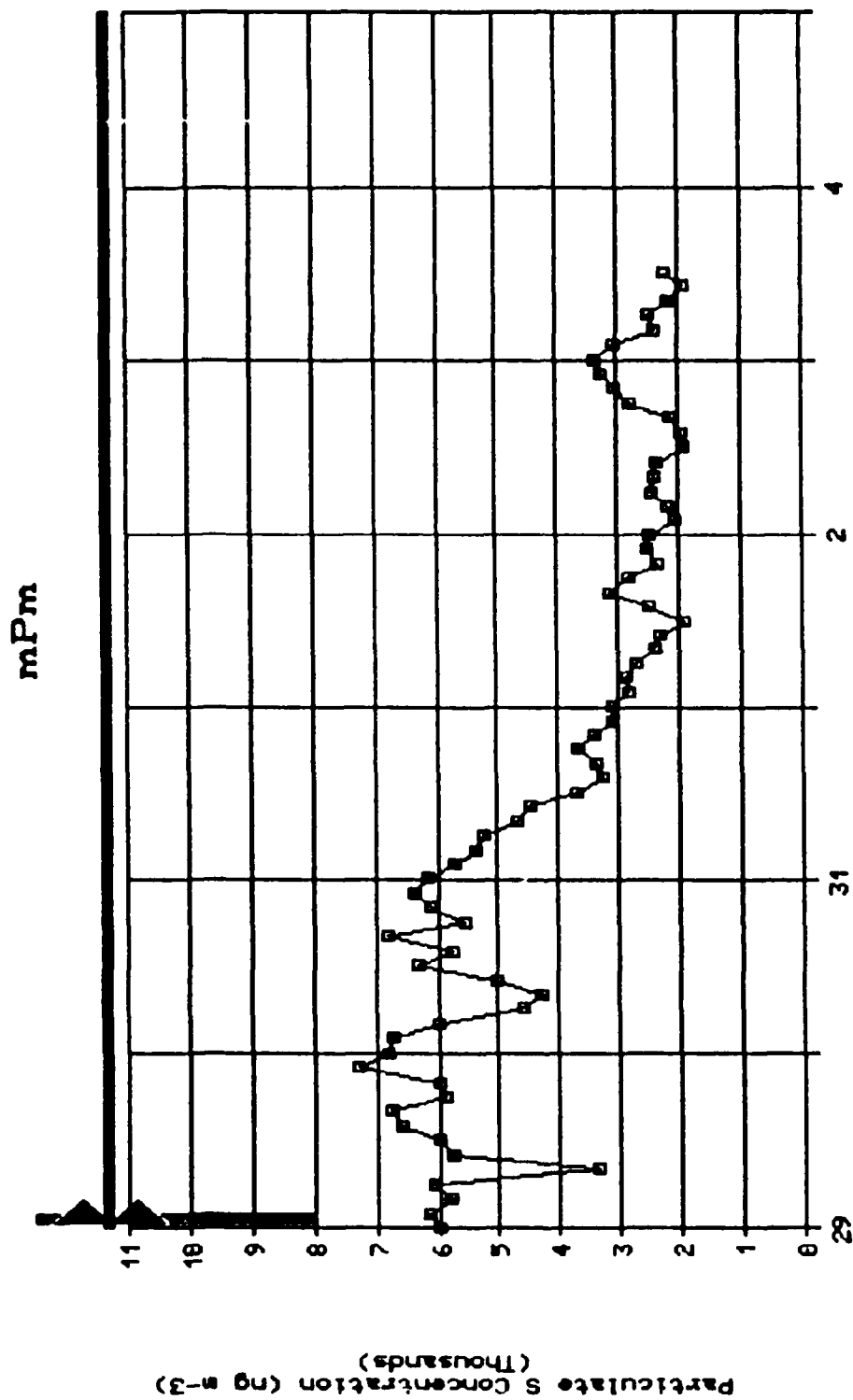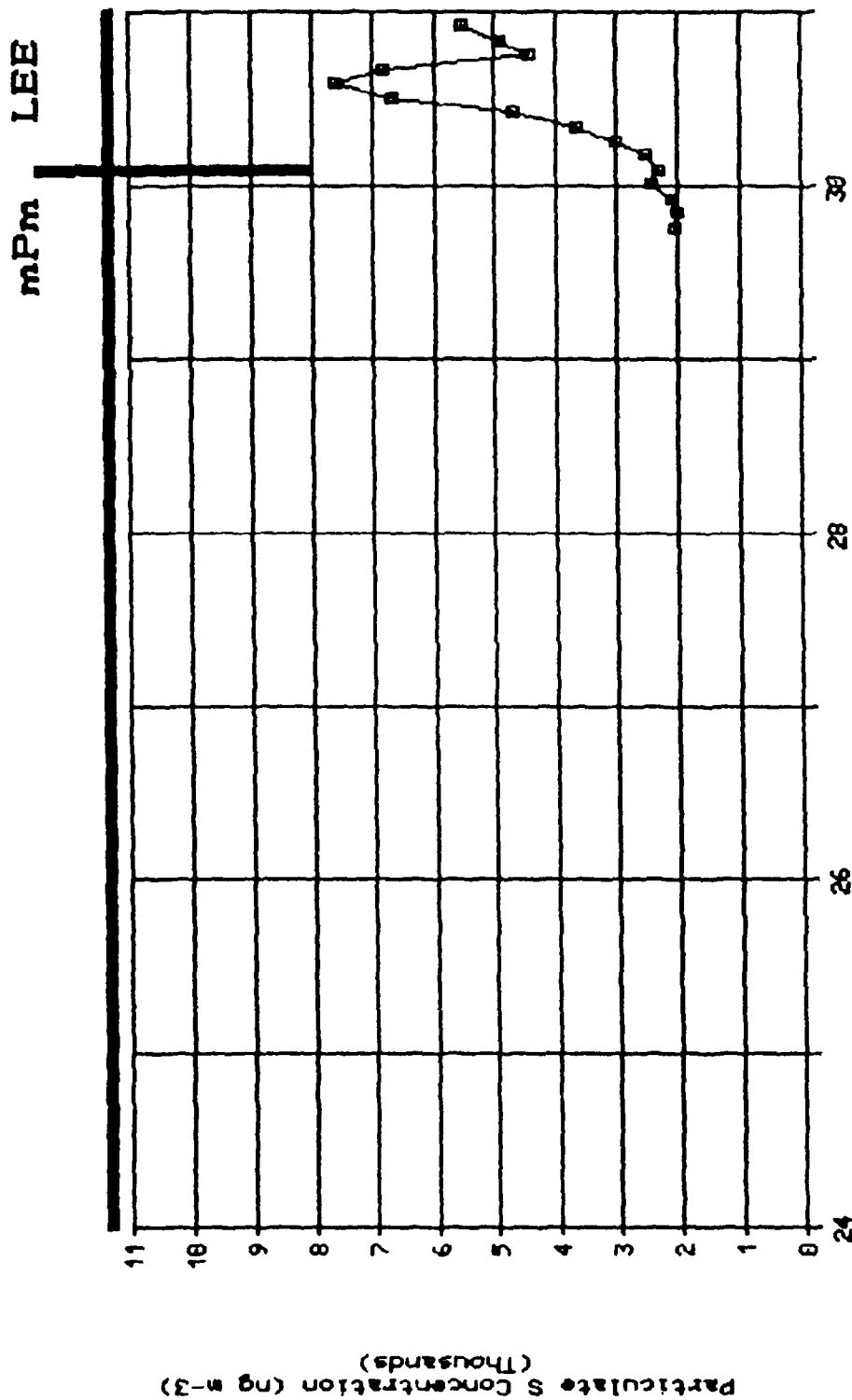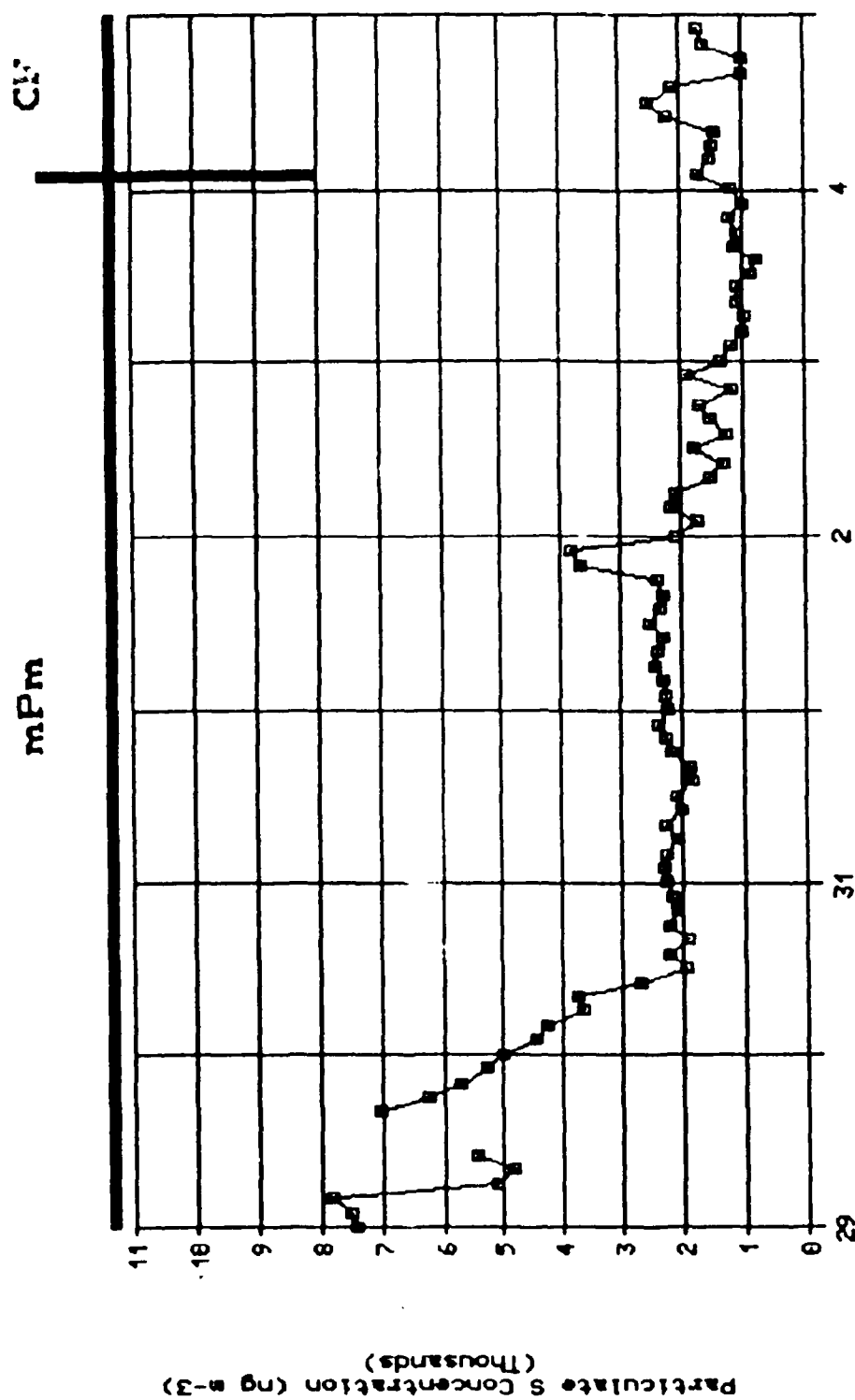Figure A.54 Atmospheric particulate sulfur concentration plotted
every 2 hours (Eastern Daylight Time) at Ft. Wayne, IN
(Site # 7) from October 29 through November 4, 1977.

APPENDIX B

Forecasting Possibilities

B.1 Introduction

Current knowledge about the diurnal variations in the concentration of APS in the eastern United States is limited, even though a large amount of data are available concerning acidic deposition. Certainly, the wet component of acidic deposition, acid rain, has a major impact on the environment as a result of precipitation events. However, dry deposition of APS occurs virtually all the time and therefore may also contribute significantly to total acidic deposition (Winchester 1983). Moreover, because of its high acidity and long residence time in the atmosphere, particulate sulfur may allow dissolution of trace metals and thereby contribute to their deposition of solubilized trace metals into human respiratory tracts and terrestrial and oceanic ecosystems (Winchester 1983, p. 295; Drummond et al. 1986; Winchester and Wang 1989; Winchester 1990).

Insight into the effects of synoptic and subsynoptic scale meteorological processes on APS concentrations developed by this thesis, as well as by others such as Grant (1989) and the SURE (Mueller and Hidy 1982b) will permit better use of current technology for monitoring and forecasting APS. Monitoring techniques currently available could be used along

with routinely available meteorological information to accurately forecast APS concentrations over a large area. These forecasts would be extremely useful in developing effective control strategies for APS. Studies such as these provide insight into what time and space scales need to be monitored to map the phenomena responsible for the bulk of APS variations. These studies show that the bulk of the concentration variations in APS occur on time scales of a few hours to several days and on spatial scales ranging down to less than 100 km. Variations on these space and time scales are not adequately resolved by coarse grid, daily averaged aerosol sampling networks.

The ability to forecast APS concentrations exists at the present time. However, routine dynamical-chemical model forecasts are not made owing to the high cost of running these models and because real-time subsynoptic scale APS concentration data is not routinely available for model initialization. As a result, neither the sizeable APS diurnal variations nor the large APS concentration changes caused by rapidly changing weather systems are forecast. Forecast efforts are further hampered by current reliance on numerical model output without the objective statistical and subjective human enhancements which have been found essential to forecasting non-chemical weather elements (Crowley 1981).

Statistical enhancement of NWP forecasts has a long and successful history for most weather elements (Glahn 1971;

Carter et al. 1989). The statistical approach has been adopted for weather elements ranging from surface dew point to precipitation amount, precisely because the best available NWP models do not incorporate all of the process which affect them. This same situation of missing processes (in this case atmospheric reactions) is found in current dynamical air chemistry models (Seaman 1990). Thus, there is every reason to expect that similar levels of forecast improvement would result from application of these techniques.

Human forecasters have proven able to improve on both NWP output and statistical guidance for most weather elements (Crowley 1981). Human forecasters benefit from the ability to use pattern recognition and conceptual models to add subsynoptic scale details to the output of larger scale models. They are also able to recognize and correct many position errors for weather systems in numerical forecasts. If provided with adequate conceptual models, humans should be able to extend this ability to the forecasting of particulate sulfur concentrations.

The remainder of this paper is devoted to discussion of those monitoring and forecasting techniques most suitable for adaptation to the problem of synoptic and subsynoptic scale APS concentration forecasting. Methods for enhancing the subsynoptic scale information content of APS analyses created from sparse monitoring networks are outlined in section B.2. Possibilities for application of both statistical and human

weather forecasting techniques to this chemical forecasting problem are discussed in section B.3.

B.2 Monitoring Possibilities

Monitoring networks of aerosol sulfur do not presently exist on a scale similar to the current acid rain monitoring network. Most of the aerosol sulfur data collected both in the past and at present comes from relatively short-term field studies rather than from long-term data collection networks. Much of the variation of particulate sulfur concentrations occurs on subsynoptic scales which are undersampled by many of these studies. Moreover, these data are typically analyzed at a later date and hence are not available for depiction of current conditions as an aid to forecasting. The primary reasons for these sampling problems are the expense of the sampling devices as well as that of the analysis of collected samples.

This thesis uses data from a special field effort which employed high time resolution sampling with relatively coarse spatial resolution to characterize synoptic and subsynoptic particulate sulfur concentration patterns. The data was represents 2-hour average APS concentrations from a synoptic scale network in the northeastern United States. The high temporal resolution permitted the identification of major particulate sulfur concentration features with time scales of

well less than a day. These features often occurred on too small a spatial scale to be resolved by the network at any one time. However, they were generally coherent, appearing in a similar form at one station after another as the controlling weather systems moved across the country. The weather systems responsible for most of the observed variations in APS concentration were on the synoptic and subsynoptic scales. Their time scales ranged from a few days to a few hours and their spatial scales ranged from a few thousand km to less than 100 km. Thus, in order to adequately monitor the majority of APS concentration variations, data must be available at temporal and spatial resolutions of a few hours and 100 km, respectively. Various strategies for obtaining data of this resolution are discussed below. By utilizing sophisticated analysis techniques adapted from other branches of meteorology, it should be possible to achieve high spatial resolution analyses without deploying sampling devices in a high spatial resolution network.

The brute-force technique for achieving the subsynoptic resolution required to capture the bulk of the APS concentration variations would require a 3-to-6 hour sampling frequency at stations spaced approximately every 100 km across most of the United States. This station density is approximately the same as that of the current National Weather Service and Federal Aviation Administration meteorological observing network of approximately 1200 stations. The total

number of stations needed in this approach is apt to be prohibitively expensive.

A more efficient method of achieving the required spatial resolution is to use the time/space conversion technique (Lewis 1982). In this method, the variable being analyzed is assumed to be approximately conserved along a trajectory for short-time scales. The data from the previous few observations are then plotted at the positions to which the observed winds are calculated to have carried the sampled air masses. Using this approach, spatially displaced data from several sequential observation times are used to fill the gaps between sample sites. For application of this approach to particulate sulfur, concentration data collected at 1-to-3 hour time intervals would be plotted along trajectories computed from the operational high density array of hourly wind observing stations. Because of limitations imposed on the usable trajectory length by the assumption of no chemical evolution, this approach would only relax the sample site spacing requirements to approximately 200 km. Nonetheless, this approach offers the advantage of greatly reducing the number of sampling sites required for subsynoptic-scale analysis, thus greatly reducing the cost of the monitoring program.

Even the assumption of conservation of APS on time scales of a few hours can be avoided by using the four-dimensional data assimilation approach instead of time/space conversion.

This approach uses a dynamical model integration to assimilate collected data from a relatively sparse network at a number of sequential sample times (McPherson 1975; Kanamitsu 1989). The model is first initialized with data from one sample time and then integrated forward in time until the next sample time when its forecast is adjusted back towards the new observations. This adjusted forecast is used as initial conditions for further integration. The cycle of integration and data insertion is continued until a high quality subsynoptic analysis is achieved. The net effect of four-dimensional data assimilation is similar to that of the time/space conversion method except that the full dynamical and chemical equations of the model are used to compute the trajectories and the evolution of the chemical composition of the sampled air as it moves along them.

Current meteorological applications involve assimilation of data with high temporal resolution and low spatial resolution into a subsynoptic scale NWP model. Such models are conceptually identical to the dynamical-chemical models described Seaman (1990) except that water is the only trace species considered. Stauffer and Seaman (1990) have achieved encouraging results with four-dimensional data assimilation of purely meteorological data. In particular, Stauffer and Seaman (1990) have shown that assimilation of hourly data from a limited number of sample sites can greatly increase the subsynoptic scale information content of a meteorological

analysis. It is expected that the approach should retain its validity with additional chemical species added to existing models. Thus, current dynamical-chemical models are suitable for implementation of four-dimensional data assimilation. This type of analysis requires a monitoring program with a sampling interval of approximately 3 hours and station separations of approximately 400 km. Analyses of the subsynoptic APS concentration pattern created by four-dimensional data assimilation would represent not only state of the art monitoring products but also high quality initial conditions for forecasts by dynamical-chemical models.

B.3 Forecasting Possibilities

B.3.1 Statistical Techniques

Objective statistical guidance has assumed an increasingly important role in meteorological forecasting over the last three decades (Shuman 1989). During this period, a broad family of techniques, ranging from automated pattern recognition to regression analysis, have been developed and refined. We will focus our attention on those techniques which have proven most successful in the operational meteorological environment. The possibilities for adaptation of these techniques to particulate sulfur concentration forecasting are discussed below.

Regression analysis has proven to be a very useful method for developing equations relating easily forecast variables to those which are more difficult to forecast (Carter et al. 1989). The exact method used depends on the type of information available in the developmental data set.

The model output statistics (MOS) method requires a developmental database containing approximately two years of both the NWP model forecast of the proposed predictor variables and simultaneous observations of the predictand variable (Glahn 1972). In the case of APS concentration, acquisition of this database would require either the collection of new APS concentration observations in parallel with operational runs of a NWP model or the rerunning of the operational numeral weather prediction model for historical cases for which APS concentration data were available. Either approach is apt to be rather costly. Linear or logistic regression analysis is then applied to derive an equation relating the predictors to the predictand. In order to generate a statistical forecast of the predictand variable, the values of the predictor variables are obtained from the operational NWP model output and inserted into the previously derived regression equation

The perfect prognosis method requires only observations in the developmental database. In the perfect prognosis method, observations of the predictor variables are used as surrogates for the NWP forecasts of these variables during

development of the regression equation. Thus, the perfect prognosis method develops a regression equation between reality and reality, whereas MOS develops a regression equation between NWP forecasts and reality. For operational use, the perfect prognosis regression equation is assumed to remain valid when NWP forecasts are used in place of actual observations of the predictor variables. The name perfect prognosis results from this assumption. The primary shortcoming of the perfect prognosis model is that it cannot correct model biases. It has, however, proven successful at accounting for processes which were missing from the NWP model formulation (Carter 1989). The primary advantage of the perfect prognosis method over the MOS method is that the costly need for simultaneous predictand observations and NWP model output for the developmental database is avoided.

The least expensive and probably least accurate form of statistical enhancement of NWP model output consists of relating a set of predictors which are available from the model to a predictand which is not available from the model. Depending on the sufficiency of the available predictors, this approach can show significant skill (Carter 1989). For the current application, either the MOS method or the perfect prognosis method could be used to develop an equation for APS concentration as a function of just those meteorological variables available from the National Meteorological Center (NMC) operational NWP models. The advantage of this approach

over those described below is that APS concentrations would not have to be monitored operationally. The disadvantage lies in the inherent assumption that the pattern of sulfur emissions is fixed over a period of a few years so that only the varying meteorological conditions affect the APS concentration pattern. To the extent this assumption is valid, this simple and inexpensive approach to statistical forecast enhancement would be successful in converting operational NWP forecasts into operational APS concentration forecasts.

One possible improvement on this approach would be to include the current APS concentration pattern in the predictor set of a MOS or perfect prognosis equation. The resulting equation would relate the current APS concentration and the forecast meteorological conditions to the future APS concentrations. The addition of APS concentration observations would eliminate the need to assume a fixed sulfur emission pattern at the cost of implementing an operational APS monitoring network. The meteorological predictors would provide the information needed to account for advection of APS and many of the chemical transformations resulting in changes of APS concentration. Monitoring of the other chemical species which are important in sulfur chemistry for use as predictors would further improve resulting APS concentration forecasts.

The most sophisticated regressive methods use forecasts

of the desired predictand as well as other forecast meteorological variables as predictors. This approach requires the output of an operational numerical model which explicitly handles the variable to be predicted. Such meteorological variables as temperature and rainfall are forecast in this manner by NMC (Carter 1989). The resulting MOS or perfect prognosis equations are used to tune the numerical model forecasts of the predictand. This approach has been particularly successful at correcting model biases and accounting for processes neglected in the numerical model. Application of this approach to the problem of APS concentration forecasting will require the operational use of a dynamical-chemical model which explicitly predicts APS concentrations. Such models currently exist, however their complexity and requirement for extensive computer time currently make them too expensive for routine forecasting (Stauffer 1990, p. 5). The operational implementation of a statistical forecast enhancement of such a dynamical-chemical model is, however, a realistic goal for forecasting APS concentrations in the future.

Artificial intelligence (AI) methods such as those described by Conway (1989) are beginning to provide an alternative to traditional regression type statistical forecast enhancements. Artificial intelligence methods have shown skill in forecasting regional heavy rains (Dai et al. 1987) by accounting for the nonlinear interactions between

predictor variables. Because of the inherent nonlinearity of many of the chemical processes which affect APS concentrations, this approach is apt to prove superior to the regression approaches to APS concentration forecast enhancement. Existing methods can be used to develop relationships between the desired predictand and any combination of observed or forecast predictors. For example, a decision tree could be developed to forecast APS concentrations from current observations alone. Alternatively, a decision tree could be developed to fine tune the output of a dynamic-chemical model. Because of their adeptness at handling nonlinear interactions, artificial intelligence methods are likely to show greatest superiority over regression methods in the first case, where chemical-dynamical model output is not available for use as predictors.

B.3.2 Role of the Human Forecaster

Human forecasters have demonstrated skill at forecasting a number of meteorological variables for well over a century. Initially, forecasters relied solely on their insight into atmospheric dynamics and cloud physics to issue forecasts based on meteorological observations. During the 1950's operational synoptic scale NWP models began to exhibit significant forecast skill through integration of the

equations of atmospheric dynamics using initial conditions derived from meteorological observations (Shuman, 1989). With this development, the role of the human forecaster shifted to oversight and adjustment of model forecasts to correct model biases and enhance model output by accounting for subsynoptic-scale phenomena. The skill of the human forecaster using model guidance has remained greater than that of the unenhanced model forecasts in subsequent decades (Crowley 1981).

The advent of regression-type statistical guidance derived from NWP model forecasts has provided yet another tool for human forecasters. This improved guidance has not eliminated the role of humans in weather forecasting as the current regression models are neither sophisticated enough to correct all model biases nor able to account for the effects of all subsynoptic weather phenomena. The ability of humans to consider complex interactions between predictands has contributed greatly to their continued edge over regression type statistical guidance. The human forecaster retains the skill advantage over numerical and statistical guidance primarily on the subsynoptic scale of 0 to 24 hours. Because large variations in APS concentration occur on this scale, the human forecaster, using conceptual models, can probably contribute significantly to the forecasting of APS concentration patterns.

Observational air chemistry studies are beginning to

provide useful conceptual models (such as the one developed by Grant, 1989) which forecasters can use to better predict the future state of the atmosphere, both meteorologically and chemically. The minimum data requirement for this type of APS concentration forecasting is the current meteorological forecasts and conceptual models APS concentration responses to synoptic and subsynoptic weather phenomena. Given these tools the forecaster can select the conceptual model which matches the predicted weather phenomena and issue the corresponding APS concentration forecast. The primary limitation of this technique is the case-to-case variability of APS concentration for similar weather events that cannot be forecast because the initial APS pattern is not known.

Knowledge of the current APS concentration pattern via timely monitoring would permit use of conceptual models relating weather phenomena to changes in APS concentrations rather than absolute concentrations of APS. The case to case variations of the observed APS concentration pattern would provide some insight into the expected differences in APS concentration associated with similar weather systems. Thus, the combination of NWP model output and timely APS concentration observations from a monitoring program such as that discussed in section 4.2.2 would allow the forecaster to show skill in APS concentration forecasting.

As both NWP APS concentration forecasts and statistical APS concentration forecasts become routinely available the

human role in pattern recognition will become a means of both correcting biases and timing errors in the model output, and of inserting subsynoptic scale details which result from processes not incorporated into the models. In this process, humans would be filling the same role in APS concentration forecasting that they currently do in weather prediction.

Detailed methodologies which allow human forecasters to recognize synoptic scale weather systems and their effect on APS concentration currently exist. This paper has examined APS concentration variations for approximately one month of data in the northeastern United States and reviewed limited studies conducted by others. Variations of APS concentration, in response to differing weather regimes and events, are clear. However, we do not know the APS concentration variations for every season or location. This study has yielded some forecasting rules for estimating APS concentration and its variations in response to differing atmospheric conditions in the northeastern United States during the fall. These forecasting rules are outlined below.

B.3.3 Forecasting Rules

Diurnal effects: Diurnal effects are most evident in anticyclones. Minimum concentrations of APS occur between 0000 and 0800 local time while concentration maxima occur between 1200 and 1600 local time. Concentration levels of APS

usually increase 1,000 to 3,000 ng m^{-3} from the morning concentration minimum to the afternoon concentration maxima. During warmer, sunnier days APS concentrations vary faster and with a larger magnitude than during cooler, cloudier days.

Anticyclones: Concentrations of APS are approximately 30% to 50% higher in mP_a anticyclones than in cP anticyclones. Concentrations of APS typically increase 50% to 100% from the eastern to western edges of anticyclones. The largest increases typically occur at continental locations while smaller increases occur at coastal locations. Superimposed on these increases are the diurnal effects.

mP_a Anticyclones - Continental locations: mP_a anticyclones whose centers pass over an inland station typically yield concentration increases of approximately 100% from their eastern to western edges. If the cyclone center does not pass over the station then APS concentration increases of only 25% to 50% are likely from the eastern to western edge of the mP_a anticyclone.

mP_a Anticyclones - Coastal locations: mP_a anticyclones whose centers pass over a coastal station typically yield concentration increases of approximately 50% from their eastern to western edges. Increases are more likely to be only 10% to 30% from the eastern to western edge of the mP_a anticyclone if the cyclone center does not pass over the station.

cP Anticyclones - Continental and Coastal locations: cP

anticyclones at both continental and coastal location fail to exhibit significant diurnal cycles. These cyclones exhibit increases in APS concentration from their eastern to western edges. However, the increases are only 20% to 30% of the initial concentration and occur in a similar manner at both continental and coastal locations.

Cyclones: Cyclones do not typically exhibit significant diurnal APS concentration variations. However, cyclones exhibit large and rapid variations in APS concentration as a result of large amounts of air mass deformation, complicated variations in vertical mixing, and complex precipitation patterns which remove APS in varying amounts. Forecasting APS concentration variations in cyclones is therefore much less accurate than forecasting APS variations in anticyclones. Cyclones typically exhibit higher APS concentrations on their eastern than western sides, with the most rapid APS concentration changes occurring across fronts, which are frequently associated with cyclones. Changes in APS concentration caused by fronts will be discussed below.

LEE Cyclones: LEE cyclones have similar concentration patterns at both continental and coastal locations. Decreases of approximately 50% to 60% in APS concentration occur from the eastern edge of a LEE cyclone to the western edge of a LEE cyclore when the center of the LEE cyclone passes over a location. When the LEE cyclone center fails to pass over a location, APS concentration patterns are difficult to

forecast. The usual pattern appears to be an APS concentration decrease of approximately 30% to 40%, depending on a stations location.

NEM Cyclones: Only one NEM cyclone influenced the SURE study area during the period of this study, therefore the effect of NEM cyclones on APS concentration is far from conclusive. Concentrations of APS appeared to remain relatively constant during this event, except where heavy precipitation occurred as a result of the cyclone. In this case wet removal of APS appeared to rapidly decrease APS concentrations by approximately 50%.

SEM Cyclones: Continental locations experience APS concentration decreases of 40% to 60% from the eastern to western edges of these cyclones. Coastal locations experienced little change in APS concentrations. However, the number of SEM coastal cases investigated by this study was very limited, therefore these results may not be representative.

COA Cyclones: Only one COA cyclone influenced a purely continental location, and then only for a short time. However, during that time some of the lowest concentrations observed at the location occurred. Variations in APS concentration were similar at coastal locations and at sites 8 and 9. When these stations were under the influence of COA cyclones, APS concentrations were often extremely low, especially if the COA cyclone center was at the sampling site.

Cold Fronts: Concentration variations of APS caused by passage of a cold front were similar at all locations investigated in this thesis. Concentrations of APS rapidly climb 50% to 100%, 4 to 8 hours before cold frontal passage. Concentrations then quickly decline 70% to 90% from their peak values, 0 to 6 hours following frontal passage. APS concentrations 6 to 12 hours after cold frontal passage are, therefore, approximately 50% of APS concentrations 8 to 12 hours before frontal passage.

B.3.4 Outlook for Particulate Sulfur Concentration Forecasting

One can forecast APS concentrations for most of the northeastern United States by combining the forecasting rules discussed above with the meteorological output of existing NWP models and knowledge of meteorological events which rapidly change APS concentrations. More accurate forecasts can be made if one has knowledge of current APS concentrations. Combining statistical techniques described above with existing dynamical-chemical models could provide a further refinement to APS forecasts. A combined application of all of these techniques could provide accurate, timely and relatively inexpensive forecasts of APS concentrations throughout the northeastern United States.

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